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THE USE OF MEMBRANE ELECTRODES MADE FROM ION EXCHANGE RESINS FOR POTENTIOMETRIC TITRATION

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During the last ten years a large number of papers have been published which have been devoted to the electrode properties of membranes made from ion exchange resins. It has been shown in these papers that membranes made from cation exchange or anion exchange resins can funtion as reversible electrodes. Hydrogen and metal functions have been studied in the case of cation exchange membranes [1-10] and also the chloride [11-15], bromide [16], flouride [15] and other functions in the case of anion exchange membranes. The existence of the corresponding electrode functions in the membranes means that the latter can be used in potentiometric titrations as indicator electrodes which are, in principle, reversible with respect to any ion e.g. to F^-, NO_3^-, CH_3COO^-, Li^+, Rb^+, Cs^+, Mg^{2+}, Ba^{2+} ions etc, for which no reversible electrodes are known, or preparation of which involves considerable difficulty. In the work described here a study was made of membranes prepared from various Russian resins as indication by the precipitation method.

Many authors have used membrane electrodes for potentiometric titration. Thus Sinkha [17], using electrodes made from IONAK S-200 sulfonated cation exchange resin, and resorcinol-formaldehyde resin, titrated hydrochloric acid with sodium hydroxide, while he used anion exchange electrodes made from the multifunctional anion exchange resin IONAK A-300 and the strongly basic anion exchange resin IRA-400 for some titrations based on precipitation. The curve he obtained did not have a clearly defined potential jump or break at the end point, and it is not clear with what accuracy such a titration can be carried out.

Results of the use of membrane electrodes for potentiometric titration based on precipitation are also given in Parson's article [18]. He used technical Amberplex C-1 cation exchange membranes and anion exchange membranes made from the strongly basic anion exchange resin IRA-400 as membrane electrodes, and titrated sulfuric acid and sodium sulfate with solutions of a barium salt. The authors evaluate the titration error as ± 0.4%.

Fischer and Bancock [19] used electrodes made from inorganic materials for potentiometric titration. Thus they used a membrane made from barium sulfate for titrating sodium sulfate with barium chloride, and for titrating sulfuric acid with barium hydroxide. Sufficiently clearly defined potential changes were not obtained at the end points, however.

Bernier and Trueb [20] used an insoluble film of aluminum oxide for the potentiometric titration of halides. The error in establishing the end point was about 4%.

Experimental Technique. In order to study the behavior of ion exchange electrodes during potentiometric titration, the following ion exchange resins were used: the sulfo-cation exchange resins SBS and KU-2, the carboxyl cation exchange resin KB-4, the resorcinol-formaldehyde resin R, the anion exchange resins EDE-10 and AV-16 substituted to different extents with amino groups, the highly basic anion exchange resin AB-17 containing quaternary ammonium groups, and also the ion exchange membranes DKU-2 (ion exchange resin KU-2 cross-linked with polychlorovinyl).

Susbtitution of the mobile ions in the ionogenic groups of the resins by the requisite ions was carried out by treating the resin with appropriate solutions of acid or salt.

The electrodes were prepared by the technique adopted in the school of physical chemistry of Leningrad State University [7]. In accordance with this method some of the air-dry resin was ground in a ball mill and then sieved. The resin fraction chosen (about 200 mesh) was mixed in a definite proportion by weight with polystyrene dissolved in toluene. The mass while still unsolidified was transferred onto a foil, the toluene removed by evaporation, and the films obtained readily removed from the foil. Ten mm diameter discs were cut out of the films with a drill, the

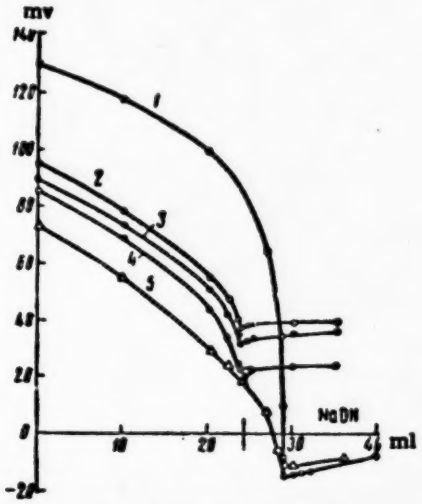

Fig. 1. Titration curves of 1 N hydrochloric acid (25 g) with 0.9572 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), KB-4 (curve 5); titration curves of 0.964 N hydrochloric acid (25 g) with 0·9572 N sodium hydroxide using electrodes made from cation exchange resins SBS (curve 4), SDV-3 (curve 2), and Ku-2 (curve 3).

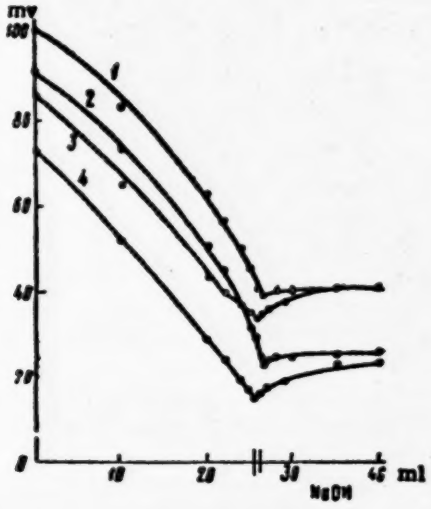

Fig. 2. Titration curves of 1.0858 N nitric acid (25 g) (curves 1 and 2) and of 0.5188 M sulfuric acid (25 g) (curves 3 and 4) with 0.9698 N sodium hydroxide using electrodes made from cation exchange resins SBS (curves 2, 4) and KU-2 (curves 1, 3).

discs were glued with polystyrene glue (a solution of polystyrene in toluene) to polystyrene tubes. The ion exchange resin content of membranes made from the cation exchange resins was 50%, while in the case of membranes made from the anion exchange resins it was 25%.

Before the ion exchange electrodes were used for potentiometric titration, they were calibrated by measuring their potentials in suitable solutions of electrolytes of varying concentration. In these experiments a silver chloride electrode was used as the reference electrode in chloride solutions, and a glass electrode in sulfuric acid solutions. The electrodes chosen were those for which the deviation of the experimental emf from the calculated value was within the limits 1-2 mv.

Potentiometric titration was carried out in a cell with 3-5 membrane electrodes whose potentials were measured with respect to a calomel electrode. The solution being titrated was measured out by weight. The 5-6 electrodes tested for each resin, as a rule, gave coincident results.

Results of Potentiometric Titration of Acids. Electrodes in the hydrogen form, made from resins differing in chemical nature, were used for titrating acids (hydrochloric, sulfuric, and nitric).

Potentiometric titration curves of 1 N hydrochloric acid using different membrane electrodes are shown in Fig. 1. The amount in ml of alkali which corresponds to the equivalent point according to titration results obtained with an indicator is marked on the abscissa. Fig. 1 shows that the shape of the curve obtained depends on the type of ion exchange resin used for preparing the membranes. The curve obtained with membranes prepared from the hydroxyl resin R (Fig. 1, Curve 1) approximates the usual potentiometric titration curve obtained with a hydrogen electrode. An appreciable potential jump is observed at the end point in this case. There is a sharp change in potential near the end point in the case of the membrance made form the carboxyl resin KB-4 (Curve 5), but there is still not a jump. The potential change near the end point is small in the case of electrodes made from the sulfo resins; the change can be established on the basis of the minimum on the curve.

Titration curves of 0.5 M sulfuric acid and 1 N nitric acid obtained on using electrodes made from the sulfo resins (SBS and KU-2) are shown in Fig. 2. The curves exhibit a clearly defined minimum at the end point, the minimum coinciding with the results of an indicator titration to an accuracy of 0.02 ml.

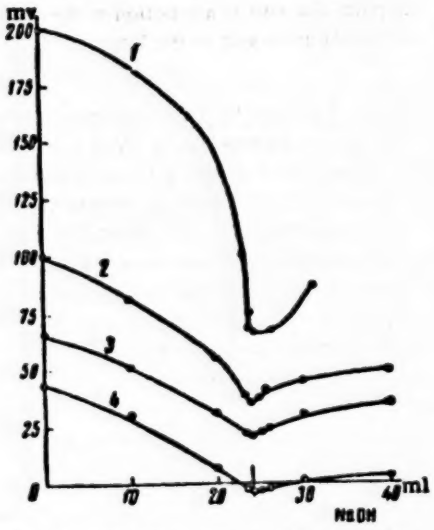

Fig. 3. Titration curves of 0.1 N hydrochloric acid (25 g) with 0.1046 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1), SBS (curve 2), KU-2 (curve 3), and DKU-2 (curve 4).

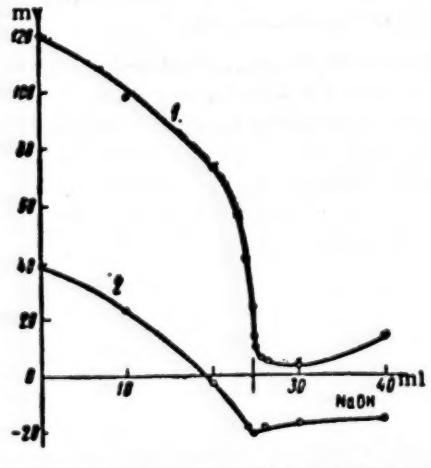

Fig. 4. Titration curves of 0.01 N hydrochloric acid (25 g) with 0.0101 N sodium hydroxide, using electrodes made from cation exchange resins R (curve 1) and SBS (curve 2).

During titration of 1 N solutions of acids, membranes in the hydrogen form were used with 0.1 N hydrochloric acid as an internal solution

Under these conditions, however, high results were obtained for 0.1 and 0.01 N hydrochloric acid when electrodes made from sulfo resins were used. The reason for the appearance of additional acidity in the solution may be the exchange of hydrogen ions from the membrane for sodium ions from the solution, which occurs during titration. In order to eliminate this effect, during titration of dilute solutions of acids electrodes made from sulfo resins were used in sodium form, while 0.1 M sodium chloride was used as the internal solution. When electrodes made from weakly acid resins are used during titration of dilute acid solution acidification of the solution following from exchange of hydrogen ions does not occur, and these membranes can be used in the hydrogen form.

Titration curves of 0.1 N hydrochloric acid using membrane electrodes made from sulfo resins in the sodium form are shown in Fig. 3. In this case the end points obtained from the potentiometric curves agree with the results obtained during titration with an indicator, while the character of the curve, as in the case of 1 N solutions, is determined by the type of resin from which the electrode is prepared.

Similar results were obtained for 0.01 N solutions of hydrochloric acid (Fig. 4). The accuracy of titration with membrane electrodes is a few tenths of a percent for all the concentrations studied.

Thus the experimental results show that membrane electrodes made from cation exchange resins in the hydrogen form can be successfully used for potentiometric titration of various acids (1-0.01 N) with alkali solutions. The character of the changes in emf during titration is determined by the acid strength of the active groups of the resin from which the membrane electrode is made. In the case of resins with weakly acid groups (the hydroxyl resin R and the carboxyl resin KB-4) there is a sufficiently sharp change in emf at the end point, corresponding to an appreciable change in pH at the titration end point (curve 1 in Figs. 1, 3, 4). The emf change from the beginning of a titration to the end point is 120-140 mv for electrodes prepared from resin R, the potential jump being 60-70 mv. For electrodes made from the carboxyl resin KB-4 the emf change up to the end point is about 90 mv (curve 5, Fig. 1). Such behavior on the part of electrodes made from weakly acid resins can be explained by the larger selectivity of these resins for hydrogen ions than for sodium ions The transition region from a hydrogen function to a sodium function, according to our results, lies within the PH range 4-7 for resin R and within the pH range 3-6 for the carboxyl resin.

The change in emf with addition of alkali in the case of electrodes made from the sufo resins can be explaind as follows. At the beginning of titration the membrane is in the hydrogen form , and its potential is determined by the hydrogen ion concentration. As alkali is added the membrane is gradually converted into the sodium form and reacts both to decreases in hydrogen ion concentration and to increases in sodium ion concentration. The nature of the curve obtained agrees with the ion exchange properties of sulfo resins, which do not exhibit selectivity toward hydrogen and other cations.

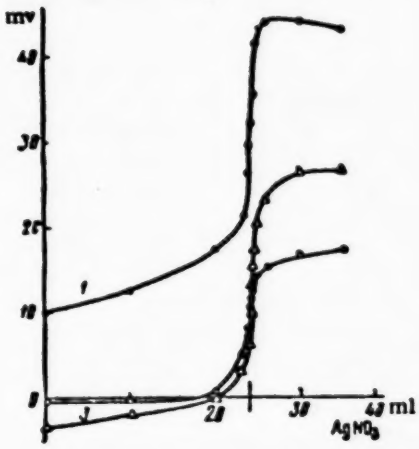

Fig. 5. Titration curves of 0.1 M sodium chloride (25 g) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins AV-16 (curve 1), and AV-17 (curve 2, 3).

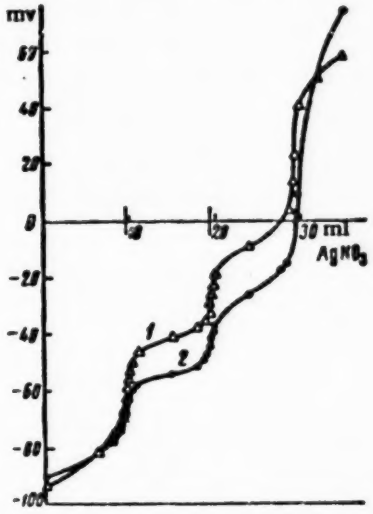

Fig. 6. Titration curves of chloride, bromide iodide (10 g of 0.1 M NaCl + 10 g 0.1 M NaBr + 10 g 0.1 M KI) with 0.1014 N silver nitrate, using electrodes made from anion exchange resins EDE-10 (Curve 1) and AV-16 (curve 2).

The transition range from hydrogen function to a sodium function lies within the pH range 1.5-3.5 [7] for electrodes made from sulfo resins. After the end point the emf is a function of the sodium ion concentration only and slowly increases as the latter increases (excess alkali).

Results of Potentiometric Titration by a Precipitation Method. Membranes made from the anion exchange resins AV-17, AV-16, and EDE-10 were used for titrating halides with a silver nitrate solution. Preliminary experiments showed that an electrolyte not containing the anion of the solution being titrated should be used as the internal solution. In the main experiments a solution of 0.05 M sulfuric acid was poured inside the membranes while a micro calomel electrode served as the internal electrode. Results of titration of 0.1 M sodium chloride with silver nitrate solution are shown in Fig. 5, from which it is clear that there is a sharp potential jump at the end point, while the position of this jump coincides with the end point determined by titration with an indicator.

The titration curves obtained with anion exchange membranes are similar in character to the curve obtained with a silver chloride electrode. The value of the potential jump at the end point in the case where membrane electrodes are used, is however, less than that obtained when a silver chloride electrode is used. In this case the change in emf up to the end point is determined mainly by the concentration of chloride ions, and not by that of NO_3^- ions, since the exchange process proceeds at a comparatively slower rate on anion exchange membranes. The chloride ion concentration changes most sharply near the end point, and the result is a sharp change in potential. After the end point only NO_3^- ions are present in solution, but the transition to the new function proceeds slowly, and, accordingly, the emf remains almost constant.

The results obtained during titration of sodium chloride with silver nitrate solution indicate that it should be possible to use anion exchange membranes for titrating mixtures of halides. The titration curves shown in Fig. 6, show that at the end points corresponding to complete precipitation of the corresponding halide, there are clearly defined jumps which correspond to the end points obtained during titration with indicators.

Anion exchange membrane electrodes in the sulfate form were used for titrating sulfuric acid and sodium sulfate with barium chloride and barium acetate solution. Titration curves of sulfuric acid with barium acetate using membrane electrodes made from anion exchange resins AV-16 and AV-17 are shown in Fig. 7. The curves obtained have a clearly defined peak which coincides with an accuracy of a few tenths of a percent with the end point obtained during indicator titration. Up to the end point the emf is determined mainly by the SO_4^{2-} concentration, which changes most sharply at the titration end point; acetate ions hardly play any part because of the low dissociation of acetic acid. In order to compare the behavior of anion exchange membranes with cation exchange membranes during titration of sulfuric acid with a barium acetate solution, cation exchange membranes in the hydrogen form made from resin KU-2 (Fig. 7, curve 3) were used. At the end point the potential of the cation exchange membrane gives a sharp minimum, the presence of which is explained by the fact that during titration the hydrogen ion concentration decreases up to the end point as a result of the formation of the sparingly dissociated acid, and the emf decreases; after the end point the emf is determined by the barium ions, and the potential increases as the barium concentration increases.

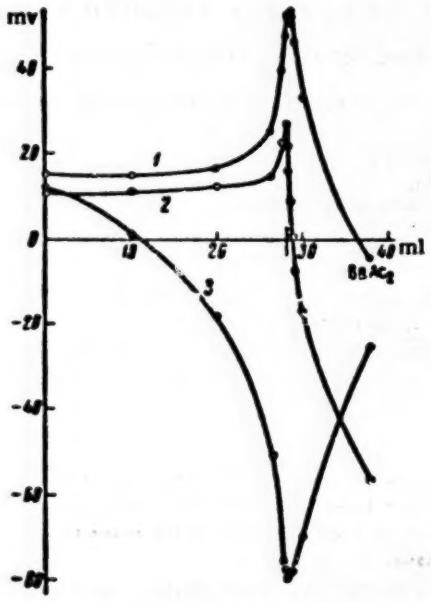

Fig. 7. Titration curves of 0.05 M sulfuric acid (50 g) with 0.1766 N barium acetate, using electrodes made from anion exchange resins EDE-10 (curve 1), AV-17 (curve 2), and cation exchange resin KU-2 (curve 3).

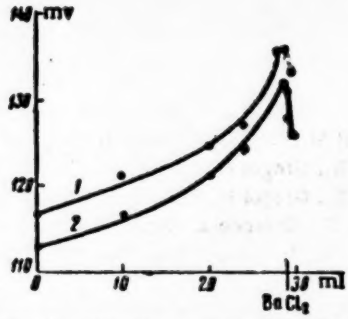

Fig. 8. Titration curves of 0.1 M sodium sulfate (25 g) with 0.1688 N barium chloride, using electrodes made from the anion exchange resin EDE-10 (curves 1, 2).

A most interesting case is titration of sodium sulfate with barium chloride solution (Fig. 8). Titration was carried out using anion exchange electrodes in the sulfate form; these electrodes react to changes in sulfate ion concentration, as a result of which there is a fairly sharp maximum peak at the end point.

SUMMARY

Membranes made from the sulfo cation exchange resins SBS, KU-2 and SDV-3, and from the carboxyl cation exchange resin KB-4 and the hydroxyl resin R, have been used as indicator electrodes for the potentiometric titration of acids. An explanation is given of the nature of the curves obtained during acid – alkali titration when membrane electrodes made from resins containing active groups differing in their chemical nature are used.

It has been established that membranes in the hydrogen form can be used for titrating concentrated acids. For titration of dilute acid solution, membranes made from the sodium form of strongly acidic resins and from the hydrogen form of weakly acidic resins should be used.

A study has been made of anion exchange membrane electrodes made from the resins AV-16, AV-17, and EDE-10 as indicator electrodes for potentiometric titration of halide and sulfate ions by precipitation methods. The curves obtained during titration of halides are similar in character to those obtained during titration with the usual electrodes which are reversible with respect to these ions. The titration curve obtained during titration of sulfate ions has a peak maximum at the end point.

The use of membranes as indicator electrodes opens up possibilities of potentiometric titration by precipitation methods.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE USE OF HYDROXY ACIDS IN POLAROGRAPHIC ANALYSIS

COMMUNICATION 1. THE HALF WAVE POTENTIALS OF CERTAIN IONS IN SOLUTIONS OF SODIUM LACTATE, MALATE AND SALICYLATE

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During a systematic study of the use of complexing agents in polarographic analysis we became interested in the behavoir of certain ions in solutions of hydroxy acids. Breda et al [1] recently published the half wave potentials of a series of ions in solutions of citric and malonic acids, in solutions of the alkali salts of these acids, and also in mixtures of 1 M sodium lactate and 1 M sodium hydroxide. The work described here is a continuation of this research; it includes results of a study of the behavior of 35 ions in solutions of lactic, malic, and salicylic acids, and in solutions of the salts of these acids at various Ph values.

EXPERIMENTAL

1 M solutions of sodium malate, lactate, and salicylate were prepared from the pure acids; after adding a solution of the salt of the test element to the solution of the hydroxy acid, the pH was adjusted to the requisite value by addition of sodium hydroxide; the concentration of the test element in the final volume was 1×10^{-3} M. Solutions of the respective salts were prepared in most cases from analytical grade materials.

TABLE 1. Half Wave Potentials of Certain Ions in 1 M Soduim Lactate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	—0,44a	—0,45f	—0,58f	—0,67a
Cu^{2+}	—0,10b	—0,30b	—0,32b	—0,36a
As^{III}	h	h	0,0c	—0,14c
Sb^{III}	h	h	h	—0,12l
Fe^{2+}	h	—1,50b	—1,51b	—1,56b
CrO_4^{-2}	—0,91a	—0,88a	—0,84a	—0,84a
Mn^{2+}	h	f	f	f
Ni^{2+}	h	h	h	f
Co^{2+}	—1,47b	f	f	f
Zn^{2+}	—1,14b	—1,30; —1,46k	—1,34; —1,53k	—1,44b
UO_2^{2+}	e	e	e	e
Ti^{IV}	—1,35e	—1,41e	—1,53e	—1,60e
MoO_4^{2-}	i	i	h	h
VO_2	h	h	—1,19e	—1,25e
In^{3+}	—0,72b	h	h	h

Note. The following ions do not give a polarographic wave Ga^{III}, As^{V}, Sb^{V}, Sn^{II}, Sn^{IV}, Pd^{II}, Au^{III}, Pt^{IV}, Fe^{II} Ge^{IV}, WO_4^{2-}, Zr^{IV}, Ce^{III}, Ce^{IV}, Be^{II} Th^{IV}, Bi^{III}, Cd^{II}.

The polarographic curves were recorded on a Heyrovski Mark V 301 polarograph, using a 30 galvanometer and a Kalousek cell with a saturated calomel electrode.

The results obtained are presented in Tables 1-3. In addition to the value of the half wave potential, a short note on the polarographic behavior of individual ions is also included.

TABLE 2. Half Wave Potentials of Certain Ions in 1 M Sodium Malate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	—0,48a	—0,49a	—0,54a	—0,67a
Cu^{2+}	—0,10a	—0,14b	—0,20b	—0,22b
Sb^{V}	—0,84; —0,98k	—0,90d	—0,93d	—0,96a
Sn^{IV}	h	h	h	—1,19d
Fe^{3+}	—0,17g	—0,37g	—0,53g	—0,82g
CrO_4^{2-}	—0,30b	—0,27b	0,28b	—0,29b
Mn^{2+}	h	f	f	f
Zn^{2+}	—1,02;—1,22k	—1,36b	h	h
UO_2^{2+}	—0,42a	0,60d	0,63d	—0,67d
Ti^{IV}	—1,3d	—1,3f	—1,3f	—1,3f
MoO_4^{2+}	—1,28d	—1,30d	i	i
VO_3^{-}	—0,04b	—0,58b	h	h

Note. The following ions do not give a polarographic wave: Ni^{II}, Co^{II}, Ge^{IV}, In^{III}, Ga^{III}, As^{III}, As^{V}, Sn^{II}, Pd^{II}, Au^{III}, Pt^{IV}, WO_4^{2-}, Zn^{IV}, Ce^{III}, Ce^{IV}, Th^{IV}, Be^{II}, Bi^{III}, Cd^{II}.

TABLE 3. Half Wave Potentials of Certain Ions in 1 M Sodium Salicylate (relative to the saturated calomel electrode)

pH	6	7	9	12
Pb^{2+}	f	f	—0,60a	—0,63a
Cu^{2+}	f	i	i	e
As^{III}	h	h	h	—0,13c
Sb^{III}	h	h	h	—0,11l
Sb^{V}	f	f	—1,14b	—1,13a
Pd^{2+}	h	—0,6e	—0,62d	—0,66d
CrO_4^{2-}	—1,18b	—1,25d	—1,10d	—0,98b
Mn^{2+}	—1,53a	—1,58a	—1,64a	—1,75a
Ni^{2+}	—1,01d	—1,04d	—1,12d	—1,17d
Co^{2+}	—1,36a	—1,37b	—1,38; —1,55d	h
Zn^{2+}	—1,20d	—1,24d	—1,32d	—1,47d
UO_2^{2+}	—0,70; —1,15k	—0,72; —1,17k	—0,74; —1,20k	—0,81: —1,22k
Ti^{IV}	—0,87; —1,70k	—0,99; —1,30k	—1,15a	—1,32a
MoO_4^{2-}	i	h	h	h
VO_3^{-}	f	f	—1,32b	—1,68b
Ge^{IV}	—1,29b	—1,31b	—1,43b	—1,59b
In^{3+}	—0,58b	—0,73b	—0,89b	—1,12b

Note. The following ions do not give a polarographic wave: Fe^{II}, Fe^{III}, Ga^{III}, As^{V}, Sn^{II}, Sn^{IV}, Au^{III}, Pt^{IV}, WO_4^{2-}, Zr^{IV}, Ce^{IV}, Be^{II}, Th^{IV}, Ga^{III}, Bi^{III}, Cd^{II}.

Notes to Tables 1-3. a) well developed symmetrical wave with a diffusion character, suitable for analytical use; b) developed wave with a diffusion character; c) readily measured anodic wave suitable for analytical use; d) poorly developed double wave; only an approximate value for the half wave potential is given, this value being the mean of the half wave potentials of both waves; e) wave difficult to measure; f) precipitate formed; g) oxidation – reduction wave; h) the ion does not give a reduction wave in the given potential range; i) a drop in hydrogen overvoltage starts; k) a double wave is formed; l) anodic wave difficult to measure.

Half wave potentials were measured relative to a saturated calomel electrode.

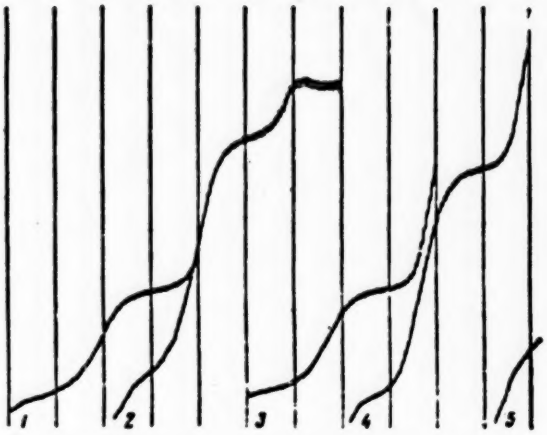

Fig. 1. Determination of nickel in cobalt. 1) 1 M sodium salicylate (9ml) + 0.01 M $NiSO_4$ (1 ml); 2) 1 M sodium salicylate (8ml) + 0.01 M $NiSO_4$ (1 ml) + 0.1 M $CaSO_4$ (1 ml); 3) 1 M sodium salicylate (8 ml) + 0.01 M $NiSO_4$ (1ml) + 1 M $CoSO_4$ (1 ml); 4) 1 M sodium salicylate (8 ml) + 0.01 M $NiSO_4$ (1 ml) + 1.55 g $CoSO_4$. Storage battery 2 v; S = 1/30; polarograms taken from −0.8 v in a nitrogen atmosphere.

Possibilities of the Practical Use of Hydroxy Acids in Polarographic Analysis. It follows from the value of the half wave potentials found that it sould be possible to use hydroxy acids in polarographic practice. An interesting example is the possibility of determining nickel in the presence of cobalt. On the basis of preliminary results it should be possible to determine nickel even at a ratio of Ni : Co = 1 : 1000 in a supporting electrolyte of 1 M sodium salicylate (pH 12-14); under these conditions nickel gives a readily measured wave, while cobalt is not reduced. Since the nickel wave depends to some extent on the presence of cobalt in solution, the method of standards should be used. The experimental error in determining nickel does not exceed the usual experimental error of the polarographic method (Fig. 1).

Another interesting example is the possibility of determining iron in the presence of high concentrations of manganese by using a supporting electrolyte of 1 M sodium malate (pH 8-9). Despite the fact that at high manganese concentrations in the given medium a precipitate is formed, the iron is not adsorbed. Fig. 2 shows some polarograms of a solution containing iron and manganese, the latter at a comparatively high concentration; the method of standard additions is used. Cu^{2+}, CrO_4^{2-}, Pb^{2+}, and UO_2^{2+} ions interfere with iron determination.

Fig. 2. Polarograms demonstrating the possibility of determining iron in the presence of manganese. Supporting electrolyte 1 M sodium malate (pH 9) (8 ml) + 1 M $MnSO_4$ (1 ml).1) Electrolyte + 1.094 mg Fe^{2+}; 2) electrolyte + 0.250 mg Fe^{2+}; 3) electrolyte + 0.469 mg Fe^{2+}; 4) electrolyte + 0.391 mg Fe^{3+}; 5) electrolyte + 1.016 mg Fe^{2+} + Fe^{3+}; 6) electrolyte + 0.047 Fe^{3+}. Storage battery 2 v; S = 1/30; polarograms taken from − 0.1 v (saturated calomel electrode) in a nitrogen atmosphere.

SUMMARY

A study has been made of the behavior of 35 ions in solutions of latic, malic, and salicylic acids, and in solutions of the salts of these acids, and their half wave potentials have been determined. The results obtained show that it should be possible to determine iron analytically in the presence of large amounts of manganese in an alkaline solution of sodium malate.

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THE COLOR OF THE INNERCOMPLEX SALTS OF BISMUTH WITH DITHIZONE AND ITS DERIVATIVES

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The method of so-called free electron gas models has proved to be the most successful approach for explaining the nature of the color of organic dyes [1-5]. Kuhn [2] has adopted this method for calculating the maximum wave length in the absorption spectra of various symmetrical and unsymmetrical organic dyes (triphenylmethane, anthracene dyes, etc). Sano [6-8] has used the method of free electron gas models for explaining the relationship between the nature of the metal – oxygen bond and the change in color of a reagent during complex formation. The author calculated the maximum wavelengths in the absorption spectra of complexes of phenylfluorone derivatives with Group IV elements, and also quantitatively evaluated the value of the polarity of the metal – oxygen bond for the phenylfluoronates of the same elements. As the ionic character of this bond increases, the absorption maximum of the metal phenylfluoronate shifts toward the longer wavelengths, i.e. toward the absorption maximum of the reagent anion.

We have applied the method indicated to the innercomplex compounds of bismuth with 1, 5-diphenylthiocarbazone (dithizone) derivatives. We calculated the maximum wavelengths of the absorption of solutions of the complexes formed between bismuth and dithizone derivatives in a number of organic solvents. The calculated values were found to be in good agreement with the experimentally determined wavelengths of the absorption maxima of the same complexes of bismuth with dithizone derivatives can be calculated when the maximum absorption wavelengths of the dithizone anion and of the anion of the corresponding dithizone derivative and bismuth dithizonate are known. The general mathematical expression for the maximum absorption is of the form:

$$\frac{hc}{\lambda_{max}} = \Delta E = \Delta E_0 + \Delta\varepsilon + \Delta\varepsilon', \qquad (1)$$

where ΔE_0 is the energy difference between the highest fundamental state and the lowest excited state of the free electron gas in the anion of the organic dye; $\Delta\varepsilon$ is a value characterizing the change in the position of the absorption spectrum of the dye which is related to the formation of a complex and is calculated from the absorption maximum of the metal complex; $\Delta\varepsilon'$ is a value characterizing the change in the position of the absorption spectrum of the dye which is caused by the introduction of a substituent into the dye molecule, and is calculated from the absorption maximum of the anion of the organic dye derivative. In our case the values of ΔE_0, $\Delta\varepsilon$ and $\Delta\varepsilon'$ are expressed as follows:

$$\Delta E_0 = h^2 (N+1)/8mcL^2 = \frac{hc}{\lambda_{\text{max of the dithizone anion}}}$$

$$\Delta\varepsilon = \left(1 - \frac{1}{N}\right) v_0 = hc\left(\frac{1}{\lambda_{\text{max metal dithizonate}}} - \frac{1}{\lambda_{\text{max of the dithizone anion}}}\right) \cdot$$

$$\Delta\varepsilon' = 4v_1 a/L = hc\left(\frac{1}{\lambda_{\text{max anion of the dithizone derivative}}} - \frac{1}{\lambda_{\text{max of the dithizone anion}}}\right) \cdot$$

where N is the number of π-electrons in the chain of the dithizone molecule ($N = 2j + 2$, where j is the number of double bonds in the chain of the dithizone molecule), m is the mass of an electron, c is the velocity of light, h is Planck's constant, L is the length of the chain of the organic dye, v_0 is the potential energy of the movement of π-electrons along the chain L; v_1 and a characterize the change in potential energy of the π-electrons on introducing a substituent into the molecule of the organic dye••. From equation (1), by substituting the value of each member, we obtain the following simple relation for calculating the absorption maximum of solutions of the complexes of bismuth with dithizone derivatives:

• The formula given in [7] is incorrect.

•• For the physical significance of v_1, a, v_0, etc see [2, 6].

$$\frac{1}{\lambda_{max}} = \frac{1}{\lambda_{max}} \text{ of bismuth dithizonate} + \frac{1}{\lambda_{max}} \text{ of the anion of the dithizone derivative} - \frac{1}{\lambda_{max}} \text{ of the dithizone anion} \quad (2)$$

Our problem consisted, therefore, in finding the absorption maxima of the anionic forms of dithizone, of its derivatives, and of bismuth dithizonate, and calculating by means of formula (2) the absorption maxima of solutions of the complexes of bismuth with dithizone derivatives in an organic solvent.

EXPERIMENTAL

Reagents. 1. The stock solution of bismuth nitrate was prepared by dissolving analytical grade $Bi(NO_3)_3 \cdot 5H_2O$ in dilute nitric acid. The concentration of the solution was established by three gravimetric methods: phosphate, 8-hydroxyquinoline, and ammoniacal methods [9]. One ml of the solution prepared was found to contain 20.82 mg Bi. Working solutions were prepared by suitable dilution of the stock solution.

2. Dithizone was purified by Markova's method [10].

3. The dithizone derivatives were prepared by formazyl method [11-13].

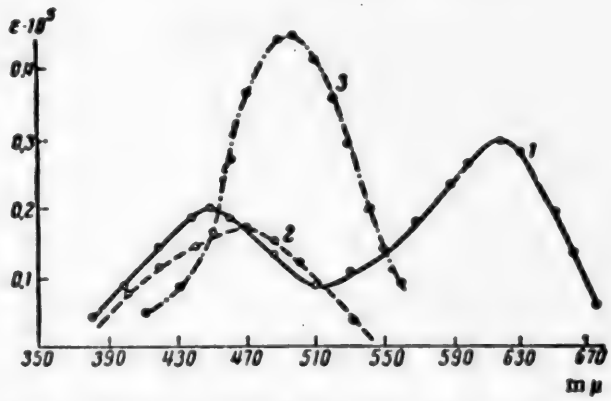

Fig. 1. Absorption spectra of the anionic (Dz^-) and molecular (HDz) forms of dithizone and of its complex with bismuth ($BiDz_3$). 1) HDz in CCl_4; 2) Dz^- in 0.7 M NaOH; 3) $BiDz_3$ in CCl_4.

The solutions of the thiocarbazones in organic solvents had a concentration of $1 \cdot 10^{-4}$ M.

4. The organic solvents were purified by distillation and their purity checked by refractive index n_D^{20} measurements.

5. NaOH, 0.7 N solution.

The optical density of the solutions was measured on a SF-4 spectrophotometer using cylindrical cells with l = 4.11 mm, relative to the pure solvent.

We obtained the absorption spectra of solutions of the thiocarbazones and of their complexes with bismuth in organic solvents, and also the absorption spectra of the anionic forms of the thiocarbozones in 0.7 N sodium hydroxide. Extraction of bismuth with the thiocarbazones was carried out at the optimum pH value of 6-8 which we had established earlier.

In Figs. 1 and 2 are shown the absorption spectra of solutions of dithizone and of p-tolylthiocarbazone in their ionic (in 0.7 N NaOH) and molecular (in CCl_4 solution) forms, as well as the absorption spectra of solutions of their complexes with bismuth. The absorption spectrum of the complex is intermediate between the absorption spectra of the corresponding thiocarbazone in its ionic and molecular forms (here and for the rest of the article, when we refer to the molecular form of thiocarbazone we shall only have the ketonic form in mind).

The difference in the absorption maxima of the thiocarbazones in their acid and alkali forms lies within the range 150-160 mμ. (Table 1).

TABLE 1. Absorption Maxima of Thiocarbazones in their Acid (Ketone) and Alkali Forms (mμ)

Reagent	Acid form, λ_1, mμ	Alkali form, λ_2, mμ	$\lambda_1-\lambda_2$, mμ
1,5-Diphenylthiocarbazone	620	470	150
p-Tolylthiocarbazone	632	480	152
o-Tolylthiocarbazone	630	470	160
β-Naphthylthiocarbazone	660	500	160
α-Naphthylthiocarbazone	665	500	165
p-Chlorothiocarbazone	635	480	155
p-Bromothiocarbazone	638	480	158
p-Iodothiocarbazone	645	490	155
o-Iodothiocarbazone	640	475	165
p-Anisylthiocarbazone	640	485	155
o-Anisylthiocarbazone	645	490	155
p-Nitrothiocarbzone	•	505	–

• p-Nitrothiocarbazone is represented in solution only as the enol form with a maximum absorption at 455 mμ.

Table 2 contains the absorption maxima of the complexes of bismuth with dithizone derivatives calculated by means of formula (2) and found experimentally for solutions in carbon tetrachloride, benzene, and chloroform; the absorption maximum of the complex of bismuth with p-nitrothiocarbazone is given for its solutions in nitrobenzene.

In the case of the thiocarbazones studied therefore, we observe a phenomenon which is contrary to that observed in the case of other known organic reagents: the anionic form of most known organic dye-reagents has a deeper color than the acid form. Since, during complex formation, a radical – metal bond develops which is more polar than the radical – reagent -H bond (i.e. the ionic character of the bond increases), the complex has a deeper color than the acid form, and a less intensecolor than the alkali form of the reagent. In the case of the thiocarbazones on the other hand the anionic form has a less intense color than the acid (ketonic) form, and complex formation leads to a shift in the absorption maximum of the acid form of the reagent toward the short wave side of the spectrum.

It is clear from Tables 1 and 2 that the shift in the absorption maxima of the complexes of bismuth with thiocarbazone with respect to the anionic form of the reagent is a constant, in all cases equal to 20-25 mμ. The innercomplex salts of bismuth with dithizone and its derivatives are more intensely colored than the color of the corresponding reagent in the anionic form, thus: a yellow colored anion corresponds to an orange colored complex (dithizone, o-tolylthiocarbazone), an orange colored anion corresponds toa red-rose colored complex (p-tolyl, p-, o-anisyl-, p-iodothiocarbazones), while a rose colored anion corresponds to a raspberry colored complex (α- and β-naphthylthiocarbazones).

In order to compare the color of solutions of the innercomplex salts of bismuth with the thiocarbazones with that of the corresponding solid salts, we prepared the salts of bismuth with dithizone, β-naphthyl-, p-tolyl-, and

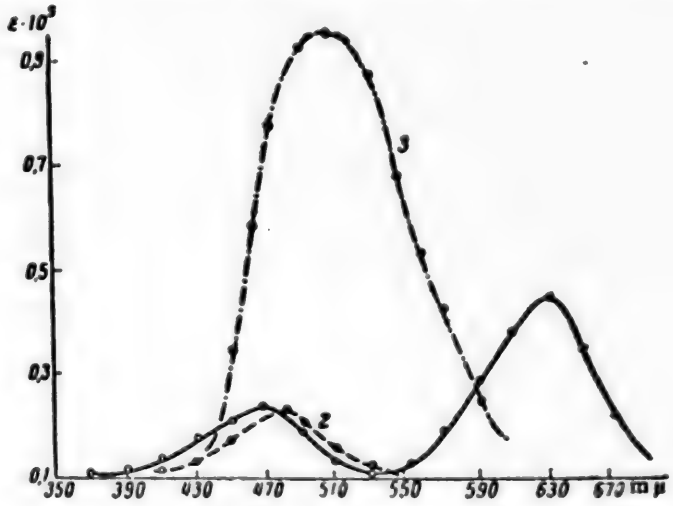

Fig. 2. Absorption spectra of the anionic (R^-) and molecular (HR) forms of p-tolylthiocarbazone and of its complex with bismuth (BiR_3) 1) HR in CCl_4; 2) R^- in 0,7 M NaOH; 3) BiR_3 in CCl_4.

TABLE 2. Absorption Maxima of Solutions of the Complexes of Bismuth with Derivatives of 1,5-Diphenylthiocarbazone (Dithizone) (A) (the Experimentally Determined Absorption Maximum of Bismuth Dithizonate in CCl_4, $CHCl_3$, and C_6H_6 was Found at 4950 A, while in Nitrobenzene it was found at 5000 A)

Reagent / Solvent	CCl_4		C_6H_6		$CHCl_3$		Nitrobenzene	
	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated	λ_{max} found	λ_{max} calculated
p-Tolylthiocarbazone	5050	5055	5050	5055	5050	5055	–	–
o-Tolylthiocarbazone	4900	4950	–	–	–	–	–	–
β-Naphthylthiocarbazone	5200	5266	5250	5266	5250	5266	–	–
α-Naphthylthiocarbazone	5200	5266	–	–	–	–	–	–
p-Chlorothiocarbazone	5050	5055	5050	5055	5050	5055	–	–
p-Bromothiocarbazone	5000	5055	–	–	–	–	–	–
p-Iodothiocarbazone	5050	5160	5100	5160	5100	5160	–	–
o-Iodothiocarbazone	4950	5002	–	–	–	–	–	–
p-Anisylthiocarbazone	5100	5107	5100	5107	5100	5107	–	–
o-Anisylthiocarbazone	5105	5160	–	–	5150	5160	–	–
p-Nitrothiocarbazone	–	–	–	–	–	–	5350	5378

p-iodothiocarbazones in the solid form according to the following methods [14].

Excess $Bi(ClO_4)_3$ was added to an acetone solution of the thiocarbazone and the mixture allowed to stand until complete deposition of precipitate had occured. The precipitate was filtered off, washed with water, and dried in a desiccator over sulfuric acid. The innercomplex salts formed between bismuth and the thiocarbazones had a metallic lustre, their color in the solid from corresponding to that in organic solvents (because of the high color intensity, in order to establish the color of the bismuth salts with the thiocarbazone, they were ground with NaCl).

The absorption maximum of a solution of the solid salt of bismuth with a thiocarbazone coincides with that of the corresponding salt obtained by direct extraction of bismuth with a solution of the thiocarbazone in an organic solvent. Comparison of the results obtained allows one to suggest that the nature of the bond between bismuth and the radical in the compounds with dithizone and its derivatives is approximately the same, both in the form of solutions in solvents of low polarity, and in the solid state.

SUMMARY

Maximum absorption wavelengths have been calculated for solutions of the innercomplex salts of bismuth with derivatives of 1,5-diphenylthiocarbazone (dithizone) in a number of organic solvents. The calculated values of the absorption maxima are in good agreement with experimentally determined values.

In order to compare the color of solid and dissolved innercomplex salts of bismuth with thiocarbazones, solid salts of bismuth with dithizone, β-naphthyl-, p-tolyl-, and p-iodothiocarbazones were prepared. The color of the solid salts and of solutions of the same salts in organic sovlents with low polarity were found to be almost identical in the case of the bismuth compounds with dithizone, β-naphthyl-, p-tolyl-, and p-iodothiocarbazones; i.e. the solid and dissolved salt are in approximately the same ionic state.

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A NEW COMPLEXOMETRIC METHOD FOR DETERMINING SULFATES IN THE PRESENCE OF CALCIUM AND MAGNESIUM

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Previously we have described several methods for the complexometric determination of barium and sulfates using sodium rhodizonate as indicator [1]. During determination of sulfates in solutions containing calcium and magnesium, the sulfates were removed as $BaSO_4$, the latter was dissolved in excess of the latter back-titrated with barium chloride solution.

In order to develop a simpler and more rapid method which would not require separation of sulfates as $BaSO_4$, we adopted Casini's method [2] as a basis, and modified it by replacing the complexometric titration based on neutralization with acid-base indicators, with complexometric titration in the presence of indicators which are specific for the ions it is required to determine in solution. The method developed permits determination of total Ca + Mg on an aliquot of test solution, titration being carried out with EDTA-Na in the presence of eriochrome black T; on another aliquot of solution, after precipitation of sulfates with a known amount of barium chloride, the total content of calcium, magnesium, and barium remaining in solution is titrated with a solution of EDTA-Na in the presence of sodium rhodizonate. In this way total Ca + Mg + Ba − SO_4 is determined. Knowing the total content of Ca + Mg, the sulfate content of the solution can be calculated.

Although the method modified in this way permits the sulfate content to be determined readily with reasonable accuracy, there is still the drawback that one had to work with another indicator and with another solution of complexon in each of the two titrations.

It has been shown earlier [1], that after dissolving the barium sulfate in excess EDTA-Na ($Na_4T + BaSO_4 \rightarrow Na_2BaT + Na_2SO_4$), on titrating excess of the complexon with barium chloride solution, also added in an amount which is in excess of that required for reaching the equivalence point, the barium sulfate is not precipitated again. Under these conditions the solution remains completely clear. When a solution containing barium sulfate dissolved in excess complexon is used for titrating any solution of barium chloride, formation of $BaSO_4$ is not observed, probably as the result of the formation of a compound containing Ba^{2+}, SO_4^{2-} ions and ethylenediaminetetraacetic acid.

The method developed for the determination of sulfates in the presence of calcium and magnesium is based on the use of this phenomenon; the method is distinguished by its rapidity and simplicity. Taking into account that the stability of the complexonates of the alkaline earth metals decreases in the series Ca > Mg > Ba, their sum can be determined by complexometric titration in the presence of an indicator for Ba^{2+} ions, sodium rhodizonate. The results obtained are accurate and reproducible (Table 1).

Table 1. Determination of $Ca^{2+} + Mg^{2+} + Ba^{2+}$ in the Presence of Sodium Rhodizonate

Content (equivalents)				Totally determined components (equivalents)
Ca^{2+}	Mg^{2+}	Ba^{2+}	Total	
0,0015	—	0,0050	0,0065	0,00650
0,0020	—	0,0050	0,0070	0,00698
0,0025	—	0,0050	0,0075	0,00750
—	0,0010	0,0050	0,0060	0,00599
—	0,0015	0,0050	0,0065	0,00650
—	0,0025	0,0050	0,0075	0,00750
0,0025	0,0010	0,0050	0,0085	0,00862
0,0040	0,0020	0,0050	0,0110	0,01101
0,0040	0,0020	0,0100	0,0160	0,01605
0,0050	0,0030	0,0100	0,0180	0,0182

* Translated from French by P. K. Agasyan.

When a known amount of barium chloride solution taken in excess is added to solutions containing calcium and magnesium in the presence of sulfates, $BaSO_4$ is precipitated in an amount corresponding to the sulfate content; further complexometric titration gives the value of total Ca + Mg + Ba − SO_4 (I).

But if a known amount of complexon solution greater than that which corresponds to the sulfate content is added to the test solution, the sulfate ions will be masked, so that on addition of excess barium chloride solution the test solution remains completely clear, as if there were no sulfate ions present at all in solution.

By continuing titration with complexon solution the value of total Ca + Mg + Mg (II) is obtained. Since the amount of barium chloride added is known, it is possible to find total Ca + Mg by difference.

The sulfate content is determined by the difference between the values II and I.

Reagents Used. 0.05N Tetrasodium ethylenediaminetetracetate solution. 9.3063 g EDTA-Na and 1.9-1.95 g of granulated NaOH are dissolved in a small amount of distilled water in a one liter standard flask, and the volume made up to the mark with distilled water. It is standardized against standard barium chloride solution.

Indicator Solution. About 20-30 mg of sodium rhodizonate is shaken up with 2 ml of distilled water. The solution should be prepared daily.

1% Alkali Blue Solution. An approximately 1% aqueous solution of alkali blue is prepared.

Buffer Solution. This consists of 200 ml of a solution containing 2 g ammonium chloride and 25 ml of a 25% ammonia solution.

Analytical Procedure. In order to check the method, two aliquots of a neutral or a weakly acid solution containing known amounts of sulfate, calcium, and magnesium are taken and diluted to a volume of about 100 ml.

A known excess of 0.05 N barium chloride (20-25 ml) is added to the first aliquot, the liquid is boiled for 2-3 min until the sulfate has been completely precipitated as $BaSO_4$, and then cooled to room temperature. A few drops of sodium rhodizonate solution is added until the characteristic rose color appears, 3 ml of buffer solution is then added, followed by alkali blue solution until the test solution has a bluish-violet color. The solution is titrated with 0.05 N EDTA-Na solution to the equivalence point, where the color of the solution changes to a pure green as a result of the superposition of the supplementary colors of the indicators [1].

The amount of EDTA-Na used up in this titration (A ml) corresponds to the content of Ca + Mg + Ba − SO_4.

To the second aliquot is added an accurately measured volume of EDTA-Na, the amount added being less than that used for titrating the first aliquot. Buffer solution is then added, followed by the same amount of barium chloride as that added to the first aliquot, and the sodium rhodizonate and alkali blue solutions. Since precipitation of sulfate is prevented in this case, titration of the completely clear solution with the standard EDTA-Na solution measured out from the same buret is continued until the color of the test solution changes to a pure green color. The total of EDTA-Na solution used in this case (B ml) is greater than the volume used in titrating the first aliquot, and corresponds to its content of Ca + Mg + Ba.

The sulfate content is calculated by means of the following equation:

$$SO_4^{2-} = (B - A) \cdot 0.0024016 \text{ g in the test material.}$$

Since the amount of 0.05 N barium chloride added to the aliquots is known, total Ca + Mg is found by difference, using the results obtained during titration of the second aliquot. The calcium, magnesium and sulfate content can be determined from the results of a complexometric titration of calcium in a new, separate aliquot of the test solution in the presence of murexide.

Table 2 contains results for the determination of sulfate in dilute solutions containing various amounts of calcium and magnesium.

Application of the Method for the Analysis of Natural Water. The method suggested has been successfully used for the determination of sulfate in drinking and industrial water, which usually, in addition to the alkali and alkaline earth metals, also contain some iron and traces of other materials which do not appreciably affect the experimental results.

The bicarbonate content, i.e. the temporary hardness, is determined first by titrating 100 ml of water with 0.1 N hydrochloric acid in the presence of methyl orange. Hydrochloric acid in an amount 0.1-0.2 ml greater than that

TABLE 2. Determination of sulfate in the Presence of Calcium and Magnesium

SO_4^{2-} content of the test sample, g	
Taken	Found complexometrically
0,00240	0,00245
0,00490	0,00492
0,00960	0,00970
0,01200	0,01200
0,04803	0,04827

TABLE 3. Determination of the Sulfate Content of Natural Water

SO_4^{2-} found, g/liter	
Gravimetrically	Complexometrically
0,03404	0,03362
0,05041	0,05043
0,05620	0,05380
0,04632	0,04528
0,05280	0,05043

used in the bicarbonate determination is added to another sample and the liquid heated for 2-3 min. After cooling to room temperature the sulfate, calcium, and magnesium content is determined as described above.

In this way the sulfate, bicarbontae, calcium, and magnesium contents are determined, as well as the hardness of the water (temporary, permanent, and total).

Results of the determination of sulfate in drinking and industrial water by the suggested method and by the classical gravimetric method are compared in Table 3.

SUMMARY

A new, rapid, and accurate method has been developed for the determination of sulfate in the presence of calcium and magnesium.

The method has been successfully used for the analysis of drinking and industrial water, and good results have been obtained; in addition, this method has the advantage that it is possible to determine total Ca + Mg by the same procedure.

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DETERMINATION OF MICROAMOUNTS OF COPPER IN WATER, SOILS, AND BIOLOGICAL MATERIALS BY MEANS OF NICKEL DIETHYLDITHIOPHOSPHATE

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A large number of methods have been suggested for the determination of copper in water, soils, and materials of plant and animal origin [1-12]. Of these methods the most widely used are photometric methods [1-4, 6-8, 10, 12], and in particular the method involving sodium diethyldithiocarbamate [4, 7, 10]. This latter reagent, however, is not specific enough and is inferior in this respect to a number of other reagents, including diphenylcarbazone [1], potassium or nickel diethyldithiophosphate [2, 13], and 2,2'-diquinolyl [3]. Comparative determination of copper by means of the three reagents indicated, in soils and plants, has shown that good results can be obtained only when the first two reagents are used. In order to determine copper by means of 2,2'-diquinolyl it is necessary to remove most of the interfering elements beforehand. In this connection therefore we have only examined in detail the two methods involving diphenylcarbazone [1] and nickel diethyldithiophosphate with respect to their application to the determination of small amounts of copper in water, soils, and biological materials.

In the course of the work described here, it was established that the presence of nitric acid in the solutions obtained after decomposition of samples of soil or plant material interferes with the determination of copper by means of nickel diethyldithiophosphate. The results obtained in the presence of nitric acid are low. Thus during determination of copper in plant material in which 10 ml of dilute nitric acid (1:2) was used for treating the ash obtained after combustion and calcining of an aliquot, the results were found to be 10-15% lower than those obtained for the same material during other experiments in which the nitric acid was removed beforehand from the solution (by adding concentrated sulfuric acid and evaporating to the appearance of white fumes of H_2SO_4). Nitric acid interferes in the same way during determination of copper in soils.

The optimum concentration of reagent added was established by making the following slight modification to the method of determining copper in soils and biological materials by means of nickel diethyldithiophosphate [2]. Busev and Ivanyutin [2, 13] have shown that one essential drawback in the determination of copper by means of potassium or nickel diethyldithiophosphate is the partial conversion under certain conditions of cupric diethyldithiophosphate into cuprous diethyldithiophosphate, this being accompanied by a drop in the intensity of the yellow color of the solution. They also established that this conversion only proceeds at an appreciable rate in the presence of appreciable concentrations of copper and potassium or nickel diethyldithiophosphate, and that when working with solutions whose copper concentration does not exceed 2 mg/liter and whose nickel diethyldithiophosphate concentration is not greater than 0.001 M, this conversion does not effect the results for copper. It was established, however, that for determination of 5-40 μg of copper, addition of 1.5-2.0 ml of 0.005 M nickel diethyldithiophosphate ensured the most reproducible and accurate results. Table 1 contains results for the determination of copper in two soil samples in which various amounts of reagent were used; they show that the amount of nickel diethyldithiophosphate indicated above is the optimum amount.

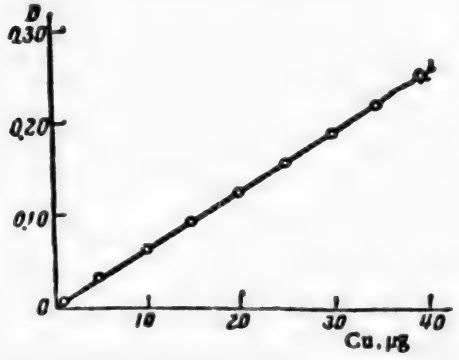
In addition to establishing the amount of reagent to be added more accurately, some other modifications were made to Busev and Ivanyutin's method [2] which enabled the time of a determination to be shortened. Copper was finally determined in soils, water, and biological materials by the following method.

For determination of copper in soils, 1-2 g of finely ground (the particle size should not exceed 0.1 mm) air-dry material is calcined in a porcelain crucible at a dark-red heat (550°) for 2 hr. After cooling, 20-30 ml of a mixture

Table 1. Accuracy and Reproducibility of the Results of Copper Determination in Soils by Busev and Ivanyutin's method [2] as a Function of the Amount of Reagent Added*

Soil Sample No. 1				Soil Sample No. 2			
Cu added, μg	Amt. of 0.005 M nickel diethyldithiophosphate sol. added ml	Cu found μg	Error %	Cu added μg	Amt. of 0.005 M nickel diethyldithiophosphate sol. added ml	Cu found μg	Error %
—	15	20,7	—	—	15	13,8	—
5	15	24,1	−6,1	5	15	17,9	−4,8
10	15	27,6	−10,1	10	15	21,6	−9,2
—	10	21,3	—	—	10	14,1	—
5	10	24,9	−5,3	5	10	18,0	−5,8
10	10	29,0	−7,3	10	10	22,1	−8,7
—	5	21,5	—	—	5	14,4	—
5	5	25,8	−2,6	5	5	18,8	−3,1
10	5	29,8	−5,6	10	5	22,9	−6,1
—	3	21,6	—	—	3	14,6	—
5	3	26,9	+1,1	5	3	19,3	−1,5
10	3	30,7	−2,8	10	3	24,3	−1,2
—	2	21,5	—	—	2	14,6	—
5	2	26,7	−0,8	5	2	19,4	−1,0
10	2	31,2	−1,0	10	2	25,0	+1,6
—	1,5	21,6	—	—	1,5	14,5	—
5	1,5	26,9	+1,1	5	1,5	19,9	+2,0
10	1,5	31,8	+0,7	10	1,5	24,1	−1,6

* In each series of three determinations the weight of soil taken was 2 g; the volume of solution after decomposition was made up to 200 ml, and 50 ml of this solution was used for each determination.



Calibration curve for photometric determination of copper.

of concentrated hydrochloric and nitric acids (3:1) is added, and the mixture is heated on a sand bath until almost all the liquid phase has been removed by evaporation. Two ml of concentrated sulfuric acid is added to the residue and heating continued until white fumes of H_2SO_4 start to come off. After cooling, 40-60 ml of water is added and the whole boiled for 10-15 min to dissolve the salts which separate out; the solution is then filtered free from the insoluble residue*. The filter is washed with hot water weakly acidified with sulfuric acid (2 ml of concentrated H_2SO_4 per 500 ml water), the wash liquors are combined with the filtrate and the copper content determined as described below.

For determination of copper in materials of plant or animal origin, a sample containing 5-100 μg copper is dried and calcined at a dark-red heat (550°). The ash is dissolved in aqua regia, the liquid is evaporated on a sand bath until almost all the liquid phase has been removed, and the procedure outlined for soil analysis then followed. The sulfuric acid filtrate which has been transferred to a 100 or 200 ml standard flask is diluted with water to the mark; 50 ml of this solution is transferred to a separating funnel**, 10 ml of CCl_4 is added, followed by 1.5-2.0 ml of 0.005 M aqueous nickel diethyldithiophosphate which is added slowly, dropwise and with stirring. The copper diethyldithiophosphate which is formed is extracted by vigorous shaking of the funnel for one minute. After the phases have separated, the organic phase is filtered through a dry filter into a cell with a path length of 1 or 2 cm, and the optical density measured on a FEK-M electrophotocolorimeter fitted with a blue filter, a blank being used as reference solution. The copper content is found by means of a calibration curve (see diagram).

* In order to filter off the insoluble material and silica more rapidly it is advisable to filter through a paper mass supported on a perforated glass plate, in a funnel, the lower part of which is filled with water.

** When the test sample contains less than 25 μg Cu, all the filtrate, without preliminary dilution in a standard flask, is transferred to the separating funnel.

Table 2. Results of the Determination of Copper in Soils, Plant Materials, and water

Test material	Copper added μg	Total amount of copper μg	Copper found μg	Error %
Black earth from Kunk, upper layer (0-10 cm) (sample wt. 1 g)	—	—	27,7	—
	5,0	32,7	32,0	−2,1
	10,0	37,7	39,0	+3,4
	15,0	42,7	41,6	−2,6
Ditto, layer taken at a depth of 30-40 cm (sample wt. 1 g)	—	—	26,6	—
	5,0	31,6	32,0	+1,3
	10,0	36,6	35,1	−4,1
	15,0	41,6	43,0	+3,4
Ditto, layer taken at a depth of 172-182 cm (sample wt. 1 g)	—	—	21,0	—
	5,0	26,0	25,0	−3,8
	10,0	31,0	30,3	−2,3
	15,0	36,0	37,5	+4,2
Clover (sample wt. 7.4 g)	—	—	28,6	—
	5,0	33,6	34,2	+1,8
	10,0	38,6	39,0	+1,0
	15,0	43,6	42,6	−2,3
Tap water, Moscow, Rublevskii Reservior (sample volume one liter)	—	—	14,7	—
	10,0	24,7	24,6	−0,4
	20,0	34,7	33,3	−4,0

TABLE 3. Results of Copper in Soils

Soil sample	Copper content found		Deviation %
	By Lapin and Makarova's method [1], %	By means of nickel diethyldithiophosphate, %	
PK-1	$4,00 \cdot 10^{-3}$	$4,04 \cdot 10^{-3}$	
	$3,80 \cdot 10^{-3}$	$3,92 \cdot 10^{-3}$	
	Mean $3,90 \cdot 10^{-3}$	$3,98 \cdot 10^{-3}$	2,1
PK-2	$3,30 \cdot 10^{-3}$	$3,36 \cdot 10^{-3}$	
	$3,02 \cdot 10^{-3}$	$3,30 \cdot 10^{-3}$	
	Mean $3,16 \cdot 10^{-3}$	$3,33 \cdot 10^{-3}$	5,4
PK-3	$3,80 \cdot 10^{-3}$	$4,10 \cdot 10^{-3}$	
	$3,97 \cdot 10^{-3}$	$4,06 \cdot 10^{-3}$	
	Mean $3,89 \cdot 10^{-3}$	$4,08 \cdot 10^{-3}$	5,0
PK-4	$3,60 \cdot 10^{-3}$	$3,84 \cdot 10^{-3}$	
	$3,85 \cdot 10^{-3}$	$3,95 \cdot 10^{-3}$	
	Mean $3,73 \cdot 10^{-3}$	$3,89 \cdot 10^{-3}$	4,3
PK-5	$3,35 \cdot 10^{-3}$	$3,48 \cdot 10^{-3}$	
	$3,23 \cdot 10^{-3}$	$3,35 \cdot 10^{-3}$	
	Mean $3,29 \cdot 10^{-3}$	$3,41 \cdot 10^{-3}$	3,6
PK-6	$2,83 \cdot 10^{-3}$	$3,01 \cdot 10^{-3}$	
	$3,02 \cdot 10^{-3}$	$3,11 \cdot 10^{-3}$	
	Mean $2,93 \cdot 10^{-3}$	$3,06 \cdot 10^{-3}$	4,4

For determination of copper in water, one liter of test water is acidified with 20 ml of 6 N H_2SO_4 and then heated at 80-100°• for 30 min. After cooling, 10 ml of CCl_4, and 2 ml of 0.005 M nickel diethyldithiophosphate are added and the whole shaken for 5 min. After standing for a short time (to enable the phases to separate) the organic layer is filtered through a dry paper filter into a cell, and its optical density measured. The copper content is determined by means of a calibration curve.

A calibration curve is constructed as follows: 0.3928 g of cupic sulfate (chemically pure grade) is dissolved in water to which 10 ml of 6 N sulfuric acid has been added, and the volume made up to the mark with water in a 1000 ml standard flask; 100 ml of this solution is transferred to another 1000 ml standard flask and the volume again made up to the mark with water. The copper content of this final solution is 10 μg/ml. Fifty ml of water and 2 ml of 6 N H_2SO_4 are added to each of 10 separating funnels; into these funnels, apart from the first, is then introduced 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 respectively of the standard copper solution (10 μg Cu/ml); finally 10 ml of CCl_4 is added to each funnel. 2.0 ml of 0.005 M nickel diethyldithiophosphate is added dropwise to each funnel with stirring, and the funnels shaken for one minute. After the phases have separated, the organic layer is filtered through a dry filter and the optical density measured (the extract from the first funnel being used as reference solution). The results obtained are plotted within the coordinates optical density – Cu content (see diagram).

When the method described above was checked on a series of soils, plant material, and water by the method of additions, it was established that the error in determining copper does not exceed 5% (see Table 2).

In addition, a series of copper determinations was carried out on six samples of soil using nickel diethyldithiophosphate and using diphenylcarbazone by Lapin and Makarov's method [1]. It follows from the results obtained (Table 3) that results of copper determination by both methods are in reasonably good agreement, nevertheless the agreement between two parallel determinations when nickel diethyldithiophosphate is used is somewhat better.

It should also be pointed out that determination of copper with nickel diethyldithiophosphate is considerably simpler and less tedious.

SUMMARY

A study has been made of the accuracy and reproducibility of the determination of copper in water, soils, and biological materials by A. I. Busev and M. I. Ivanyutin's method, using nickel diethyldithiophosphate as reagent. It has been shown that by using the reagent at a certain optimum concentration, and by removing interference from nitric acid, it is possible to reduce the error of the determination down to 5%. After the appropriate modifications have been made, the results obtained during the photometric determination of copper by means of nickel diethyldithiophosphate are superior in accuracy and reproducibility to those obtained by L. N. Lapin and V. P. Makarova's method, and at the same time are simpler and more rapid.

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•Low results are obtained if preliminary heating of the test water is omitted.

GRAVIMETRIC DETERMINATION OF SCANDIUM BY MEANS OF BENZENESELENINIC AND BENZENESULFINIC ACIDS

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Of the organic reagents which precipitate scandium, the ones used are ammonium tartrate, oxalic acid, inositol-pyrophosphoric acid (phytic), alizarinsulfonic acid, and 8-hydroxyquinoline. The reactions with these reagents have been carefully studied by Fisher and Bock [1], and later by Vickery [2] using Sc^{46}. It was established that all these reagents suffer from some disadvantages. Accordingly, a search for new organic precipitants of scandium is a necessary prerequisite for the successful solution of problems in the preparative and analytical chemistry of scandium. We have studied ammonium benzeneseleninate and benzenesulfinate as possible reagents for this purpose.

Feigl [3] was the first to suggest benzeneseleninic acid as an analytical reagent, and it has been examined by Alimarin and Sotnikov [4].

We established that ammonium benzeneseleninate forms with scanadium in neutral and weakly acid solutions, a white crystalline precipitate which is readily soluble in mineral acids. Ammonia decomposes this compound with formation of the hydroxide. The sensitivity of the reaction is 5 μg/ml. X-ray studies of the precipitate confirmed its crystalline nature (Fig. 1). According to results of chemical analysis the scandium compound corresponds to the formula $Sc(C_6H_5SeO_2)_3$, the scandium content being 7.38%. This compound can be recommended as a gravimetric form. A thermogravimetric study of the precipitate confirmed the stability of scandium benzeneseleninate at temperatures up to 120°. On heating to 600° this compound is completely converted into scandium oxide (Fig. 2).

Table 1. Determination of Scandium as Sc_2O_3

Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
		mg	%
1.23	1.20	+0.03	+2.4
1.29	1.18	+0.05	+4.0
2.46	2.49	+0.03	+1.2
2.46	2.50	+0.04	+1.6
5.90	5.82	−0.08	−1.3
5.90	5.93	+0.03	+0.1

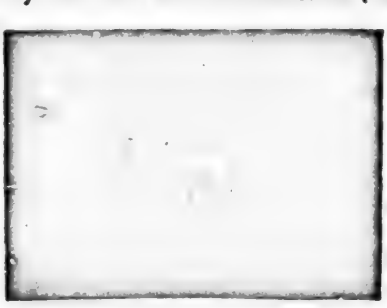

Fig. 1. X-ray spectrogram of scandium benzeneseleninate.

Benzeneseleninic acid has a number of advantages over organic reagents suggested earlier. Scandium benzeneseleninate has a low correction factor f = 0.0738, the precipitate is formed in a crystalline state in a short time (15 min), and it can be rapidly brought to constant weight by drying at 105°.

The difference in the solubility of scandium and zirconium benzeneseleninates (see [5]) has enabled us to develop a technique for determining scandium, and for separating it from zirconium.

A 20% solution of ammonium benzeneseleninate was prepared by dissolving the commercial reagent in distilled water. A scandium chloride solution was prepared by dissolving scandium oxide in redistilled concentrated hydrochloric acid on careful heating, with subsequent evaporation of the acid until the moist scandium chloride salt separated out; this was dissolved in distilled water. The concentration of the solution was established by precipitation of scandium

TABLE 2 Determination of Scandium by Weighing it as Scandium Benzeneseleninate

Wt. of $Sc(C_6H_5SeO_3)_3$, mg	Sc taken, mg	Sc found, mg	Error		Wt. of $Sc(C_6H_5SeO_3)_3$, mg	Sc taken, mg	Sc found, mg	Error	
			mg	%				mg	%
37,90	2,81	2,80	−0,01	−0,4	9,55	0,70	0,71	+0,01	+1,5
38,00	2,81	2,81	0,00	0,0	4,80	0,35	0,35	0.00	0,0
37,95	2,81	2,80	0,00	0,0	4,82	0,35	0,36	+0,01	+3,0
19,00	1,40	1,40	0,00	0,0	4,75	0,35	0,35	0,00	0,0
18,95	1,40	1,37	−0,03	−2,0	1,95	0,14	0,14	0,00	0,0
19,00	1,40	1,40	0,00	0,0	1,92	0,14	0,14	0,00	0,0
9,35	0,70	0,69	−0,01	−1,5	1,85	0,14	0,14	0,00	0,0
9,45	0,70	0,70	0,00	0,0					

TABLE 3. Separation of Scandium and Zirconium by Precipitation with Ammonium Benzeneseleninate and Using Zr^{95}

Sc : Zr	Sc_2O_3 taken, mg	Zr^{95} added, cpm	Sc_2O_3 found, mg	Zr^{95} found, cpm	Error mg
1 : 1	1,24	1270	1,20	1283	−0,04
	2,49	1270	2,49	1257	0,00
1 : 2	1,24	1270	1,21	1245	−0,03
	2,49	1270	2,45	1269	−0,04
1 : 10	1,24	1270	1,22	1235	−0,02
	2,49	1270	2,52	1251	+0,03
	4,98	1270	5,06	1274	+0,08

TABLE 4. Separation of Scandium and Zirconium by Precipitation with Ammonium Benzeneseleninate and Using Sc^{46}

Sc : Zr	Sc_2O_3 taken, mg	Sc^{46} added, cpm	Sc_2O_3 found, mg	Sc^{46} found cpm	Error mg
1 : 1	1,24	2,432	1,21	2367	−0,01
	2,49	1715	2,46	1704	−0,03
1 : 2	1,24	1933	1,19	1928	−0,05
	2,49	1920	2,50	1924	+0,01
1 : 10	1,24	2624	1,23	2240	−0,01
	2,49	2637	2,52	2250	+0,03

TABLE 5. Determination of Scandium by Precipitation with Ammonium Benzenesulfinate and Weighing as Sc_2O_3

Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
		mg	%
1,47	1,52	+0,05	+3,3
1,47	1,50	+0,03	+2,0
1,47	1,45	−0,02	−1,3
3,67	3,69	+0,02	+0,5
3,67	3,70	+0,03	+0,8
3,67	3,67	0,00	0,0
12,80	12,80	0,00	0,0
12,80	12,93	+0,11	+0,8
12,80	12,90	−0,10	−0,8

TABLE 6. Separation of Scandium and the Rare Earths by Precipitation with Ammonium Benzenesulfinate

Sc : Rare Earths	Sc_2O_3 taken, mg	Sc_2O_3 found, mg	Error	
			mg	%
1 : 1	2,37	2,20	−0,17	−7,7
	2,37	2,18	−0,19	−8,6
1 : 10	2,37	2,35	−0,02	−0,8
	2,37	2,32	−0,05	−2,1
1 : 20	2,37	2,36	−0,01	−0,4
	2,37	2,37	0,00	0,0
	4,74	4,70	−0,04	−0,8
1 : 50	2,37	2,35	−0,02	−0,8
	2,37	2,37	0,00	0,0
	4,74	4,77	+0,03	+0,6

hydroxide, and complexometric titration in the presence of murexide. Zirconyl oxychloride was dissolved in distilled water and the concentration of the solution established complexometrically.

Completeness of precipitation, and the purity of the precipitates obtained were checked radiometrically using the isotopes Sc^{46} and Zr^{95}. The latter was freed from the daughter element niobium by repeated coprecipitation of Nb^{95} with MnO_2. Sc^{46} was obtained by bombarding scandium oxide with neutrons by the reaction Sc^{45} (n, γ) Sc^{46}.

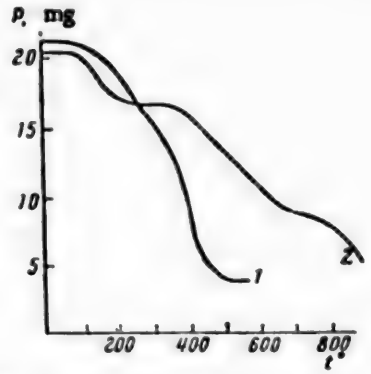

Fig. 2. Thermogravigrams of scandium benzeneseleninate (1) and scandium benzenesulfinate (2).

Fig. 3. X-ray spectrogram of scandium benzenesulfinate.

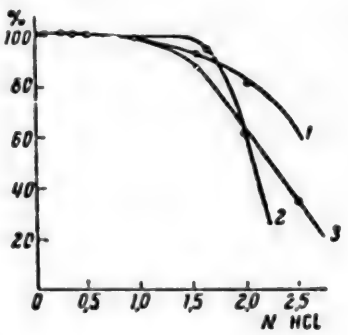

Fig. 4. Precipitation of scandium (I), zirconium (II), and thorium (III) by ammonium benzenesulfinate as a function of the acidity.

Scandium benzeneseleninate was precipitated from weakly acid solutions, 50 ml of a solution of the scandium salt was heated on a water bath, a drop of methyl orange was added and the solution neutralized with ammonia solution (1:1) to the first color change of the indicator. Five ml of ammonium benzeneseleninate solution (precipitate concentration 2% by volume) was added to the hot solution, and the mixture cooled to room temperature. Under these conditions the precipitate of scandium benzeneseleninate packed together and the solution above the precipitate clarified. Subsequently scandium can be determined either by weighing the precipitate of scandium benzeneseleninate or by calcining the latter to the oxide. To obtain the oxide the precipitate was filtered off through a paper filter and calcined at 800° for 30 min (Table 1).

For determination of scandium as the benzeneseleninate, the precipitate obtained as described above was filtered off through a glass microfilter with a No. 4 porous glass bottom, the precipitate was washed with 10-15 ml of twice distilled water and then with the same amount of ethanol; it was finally dried at 105° for 20 min (Table 2).

In order to separate scandium from zirconium the latter was precipitated from hot 1 N HCl solution with ammonium benzeneseleninate, the precipitate was filtered through a blue band filter paper, and carefully washed with 0.5% ammonium benzeneseleninate solution. The filtrate was evaporated on a water bath to a volume of 50 ml, and scandium determined by one of the methods indicated above.

Completeness of separation of scandium from zirconium was checked by means of radioactive indicators. Two series of experiments were carried out. In the first series of experiments completeness of precipitation of zirconium in the presence of scandium was controlled by means of Zr^{95}; the scandium was determined by calcining scandium benzeneseleninate to scandium oxide (Table 3). In the second series of experiments completeness of precipitation of scandium was checked by means of Sc^{46} (Table 4).

Scandium was quantitatively separated from zirconium at a maximum ratio of Sc:Zr = 1:10; at higher zirconium concentrations high results were obtained for scandium.

Ammonium benzenesulfinate has been used by Alimarin and Alikberov for the determination of zirconium and thorium [6, 7]. With scandium, in acid (down to 2.5 N) and neutral solutions, benzenesulfinic acid, and its sodium and ammonium salts form a white flocculent precipitate which is soluble in mineral acids. The sensitivity of the reaction is 2 μg/ml. X-ray studies (Fig. 3) showed that the precipitate formed has a crystalline structure. It should be pointed out that the acidity of the solution strongly affects the structure of the precipitate formed; thus in acid solutions (from 0.3 N upward) a finely crystalline precipitate is formed which is difficult to filter, while scandium benzenesulfinate formed in neutral solutions is compact and is readily filtered. A study of the compound formed confirmed that it is a normal salt with the composition $Sc(C_6H_5SO_2)_3 \cdot xH_2O$. Scandium benzenesulfinate cannot be recommended as a gravimetric form because of its variable water content. It is clear from the thermogravigram of scandium benzenesulfinate (Fig. 2) that the latter is completely converted into scandium oxide at temperatures above 800°. We have developed a method for separating scandium from the rare earths, iron, and aluminum, and for determining it

by precipitation as scandium benzenesulfinate, followed by calcination of the latter to scandium oxide. In the work described here scandium benzenesulfinate was precipitated from 50 ml of a 0.5 N HCl solution using a precipitant concentration of 1% by volume. After addition of precipitant the solution was heated on a water bath for 10-15 min. Heating above 80° should be avoided, since the precipitate separates out in a fine crystalline form and starts to creep up the vessel walls. The precipitate was filtered through a blue band filter and calcined at 1000° for 45-60 min. Scandium was determined by weighing it as its oxide (Table 5).

A study was made of the effect of the acidity of the medium on completeness of precipitation of scandium. It is clear from Fig. 4 that zirconium and thorium are precipitated by ammonium benzenesulfinate over the same acidity range as scandium. Precipitation of scandium, according to the technique indicated, in the presence of aluminum and the yttrium group of the rare earths permits scandium to be separated from the latter (Table 6).

The presence of less than 5 mg of iron in 50 ml of a solution in 0.7 N HCl does not interfere with scandium determination.

SUMMARY

Benzeneseleninic acid and its ammonium salt form a white crystalline precipitate with scandium in neutral and weakly acid solutions. The composition of the compound corresponds to the formula $Sc(C_6H_5SeO_3)_3$. The precipitate can be recommended as a gravimetric form (conversion factor to scandium 0.0738).

A method has been developed for the determination of scandium in the presence of the rare earths, iron, and aluminum by precipitating it with benzensulfinic acid. The composition of the precipitate approximates to the formula $Sc(C_6H_5SO_2)_3 \cdot xH_2O$. For quantitative determination of scandium this compound is calcined at 1000° and the scandium is weighed as Sc_2O_3.

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THERMOGRAVIMETRY IN ANALYTICAL CHEMISTRY

COMMUNICATION 3. THERMOGRAVIMETRIC STUDY OF LANTHANUM CARBONATE

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Carbonate ions have been used for a long time in preparative practice, both for coarse separation of total lanthanides from the cerium and yttrium groups [1, 2], and also for the preparation of individual rare earth elements [3-5]. The normal carbonates of the rare earths can be prepared by different methods – by passing CO_2 into a suspension of hydroxides [6], by hydrolysis of solutions of their trichloroacetates [7], and, finally, by the interaction of readily soluble salts with the alkali metal carbonates. The last method is certainly the simplest and most practicable; there is, however, no unanimous opinion regarding the composition of the sparingly soluble compounds formed in this case. The precipitates formed have been ascribed the structure of basic carbonates [8], double salts [9], or normal carbonates [10]. On the basis of our own results on the chemical analysis of lanthanum, neodymium, erbium, and yttrium carbonates [11, 12] prepared by the last method, and also on the basis of a study of the system alkali metal carbonate – trivalent cerium – water, carried out by physicochemical analytical methods [13], we are of the opinion that normal carbonates with the composition $R_2(CO_3)_3 \cdot nH_2O$ are formed over the concentration range studied when equimolar amounts of the reagents are used. The possibility of using these compounds for anlytical purposes, and, in particular, as a gravimetric form, has not apparently been examined.

No strictly quantitative results on the solubility of the lanthanide carbonates has been published. Nevertheless, tentative information on the solubility of lanthanum and neodymium carbonates [11, 12] gives ground for assuming that it should be possible to precipitate the elements of the cerium group quantitatively by means of alkali metal carbonates (as long as a large excess of precipitant is avoided, since the latter at high concentrations act as complexing agents not only for elements of the yttrium group, but also for cerium group elements).

The problem of thermal stability, particularly with respect to establishing the range over which a particular compound exists, can be reliably resolved by Duval's thermogravimetric method [14]. The results given in the present article were obtained on a thermobalance of simplified construction described previously [15, 16].

EXPERIMENTAL

X-ray structural analysis showed that the lanthanum oxide used in the present work contained 0.15% each of Pr_6O_{11} and Nd_2O_3. Other rare earths present as impurities could not be detected. Of other foreign elements only about 0.01% iron could be found. Potassium, sodium, and ammonium carbonates – chemically pure grade – were used without further purification. Chemically pure grade hydrochloric acid was redistilled. 1, 0.1, and 0.01 N solutions of $LaCl_3$ were prepared from accurately weighed amounts of La_2O_3. The concentration of the solutions was checked gravimetrically by precipitation with oxalic acid. The concentration of the solutions of the alkali carbonates (1, 0.1, and 0.01 N) was determined by titration with hydrochloric acid.

Equal volumes of lanthanum chloride solution and alkali metal carbonate solution of the same normality were mixed at room temperature and allowed to stand for two hours, after which the precipitates formed were filtered off. Subsequent treatment of the precipitates to prepare them for thermogravimetric study differed slightly in detail. Aliquots of 30 to 50 mg of the treated precipitates were used for thermal decomposition. The experimental procedure was completely identical to that described previously [15, 16].

• For communication 2, see Zh. analit. khimii 15, 706 (1960)

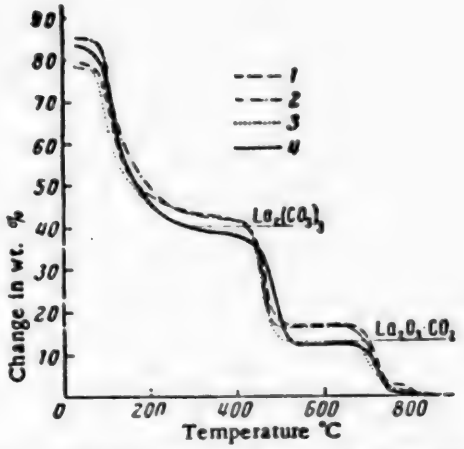

Fig. 1. Thermogravigrams of lanthanum carbonate precipitated with potassium carbonate of varying concentration. 1) From 1 N $LaCl_3$; 2) from 0.1 N $LaCl_3$; 3) from 0.01 N $LaCl_3$; 4) from 1 N $LaCl_3$, precipitate washed with water.

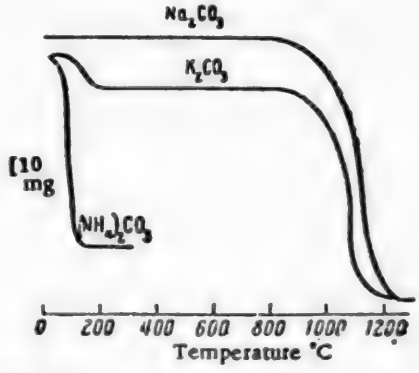

Fig. 2. Thermogravigrams of alkali metal carbonates.

It is fairly frequently stated in the literature [8] that there is a relationship between the composition of the precipitates formed in the systems rare earth^{3+} – Me_2CO_3 – H_2O (where Me is the alkali metal cation) and the concentration of the original solution. It was necessary therefore to establish whether there is such a relationship, and if there is, to what extent this factor affects the nature of the thermogravigrams obtained. Moreover, it was also necessary to define more accurately the method of preparing the sample for study. In Fig. 1 are shown thermogravigrams of carbonate precipitates obtained by precipitation of lanthanum chloride with potassium carbonate at room temperature. Curves 1, 2, and 3 correspond to precipitates obtained by precipitation from 1, 0.1, and 0.01 N solutions and filtered off by means of a water pump, without washing. Curve 4 corresponds to the precipitate obtained from a 1 N solution, but carefully washed on the filter with water.

As Fig. 1 shows, the general nature of all four thermogravigrams, after the sharp drop in the curve determined by removal of water of crystallization and hygroscopic water from the precipitate, is the same; over the range 275-400° there is an almost horizontal part corresponding, according to calculation, to the anhydrous carbonate $La_2(CO_3)_3$. This is followed by another sharp drop determined by the decomposition of the anhydrous carbonate, and a distinct area (from 500 to 650°) corresponding to the existence of its intermediate decomposition product. Calculation in this case indicates that this product has the approximate formula $La_2O_3 \cdot CO_2$. The third drop on the curve corresponds to decomposition of this compound and terminates at a temperature slightly higher than 800°. Starting from this temperature only lanthanum oxide La_2O_3 is thermally stable. There are, nevertheless, certain differences which exceed the normal errors met in thermogravimetric analysis. On the one hand, curves 1 and 2, which correspond to the more concentrated solutions, throughout their whole length lie above curve 3, which corresponds to the most dilute of the solutions used. On the other hand, curve 2 lies above curve 4, although the solutions in both cases are the same, the difference being in the preparation of the precipitates for analysis (washing).

It would appear that the simplest explanation of both these facts is hydrolysis. Actually, in the first case one could assume a higher degree of hydrolysis of the carbonate compounds obtained from the most dilute original solutions, and in the second hydrolysis of the precipitate during washing with water. One objection to this hypothesis, however, in the first place, is the thermogravigram of the precipitate obtained from 0.01 N solutions heated beforehand to 60-70°. This curve is not included in Fig. 1 since it coincides completely with curve 3. If hydrolysis had actually occured then the extent of hydrolyis of the precipitates obtained from hot solutions would be greater, and the curve mentioned above would lie below curve 3. In the second place, only the deviations on the initial parts of the thermogravigrams can be explained by hydrolysis, since there is only a very small probability that the hydrolyzed compounds can exist at very high temperatures, e.g., over the range within which the intermediate compound is stable. At the same time deviations between the curves are observed over this range too.

Another possible interpretation of the phenomena observed is the difference in the degree of entrainment by the precipitates of the reaction products (KCl) from the mother liquors when original solutions of varying concentrations are used. In fact, after removal of water from the precipitates, the KCl entrained by the precipitates remains, and is only removed at very high temperatures. All the precipitates were treated under identical conditions; accordingly their

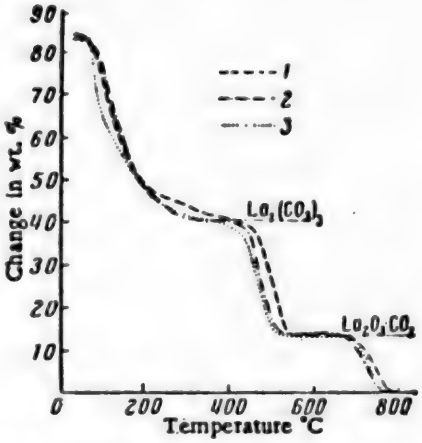

Fig. 3. Thermogravigrams of lanthanum carbonate precipitated by ammonium carbonate from solutions of varying initial concentration. 1) From 1 N $LaCl_3$; 2) from 0.1 N $LaCl_3$; 3) from 0.01 N $LaCl_3$.

moisture content is approximately the same, and the amount of salt (KCl) remaining in the precipitate should be proportional to its concentration in the mother liquor. If stoichiometric proportions are strictly observed, the initial products cannot be present in the solutions, and consequently in the precipitates; if, however, the process is used for actual precipitation of lanthanum carbonate or the carbonates of other elements of the cerium group, then naturally a certain excess of the alkali metal carbonate will be present in solution, and also in the precipitate. Bearing this in mind, the thermogravigrams of the three most readily available precipitants – sodium, potassium, and ammonium carbonates – are shown in Fig. 2.

The results of thermogravimetric analysis, as well as published information [17] on the thermal stability of the carbonates and chlorides of potassium, sodium, and ammonium indicate that ammonium carbonate should be chosen as the precipitant, since the presence of ammonium cabonate itself or of ammonium choride should not affect the composition of the gravimetric form of the anhydrous carbonates, and, in particular, that of the intermediate product obtained during the thermal decomposition of the anhydrous carbonate. The next series of experiments was carried out with ammonium carbonate. The method used was left unchanged, apart from the fact that the carbonate precipitates, after having been filtered, were dried in a vacuum desiccator to constant weight. The corresponding thermogravigrams are shown in Fig. 3. Curves 1, 2, and 3 correspond to the precipitates obtained from 1, 0.1, and 0.01 N solutions respectively.

From these results it is clear that the modifications made to the original method enable better results to be obtained. Accordingly, the main factor affecting the composition of the carbonate precipitates would appear to be contamination of these precipitates by the alkali metal chloride, and not differences in the extent of hydrolysis as a function of the concentration of the original solutions. On washing the precipitates for a long time with water, hydrolysis, apparently, also takes place (this is clear from a comparison of curve 4, Fig. 1 and Curve 1, Fig. 3); its effect is, however, small. The series of experiments also enabled us to define the temperature range over which both compounds are stable more accurately; this range is about 100° (300-400°) for anhydrous lanthanum carbonate; for the decomposition product of the latter this range is slightly wider 550-675°, the section of the curve over this range being completely horizontal. In order to confirm the composition of both compounds, the precipitates were kept at constant weight at temperatures corresponding approximately to the middle of the horizontal sections (375 and 600°), and analyzed [18]. Results of elemental analysis of both products obtained from original solutions with concentrations ranging from 1 to 0.01 N are given in Tables 1 and 2.

Table 1. Elemental Analysis of the Compound Brought to Constant Weight at 375° [Suggested composition – $La_2(CO)_3$]

Test Element*	Calculated, %	Found on precipit. from sol. of varying normality, %		
		1 N	0.1 N	0.01 N
C	7,86	7,67	7,75	7,90
O	31,44	31,56	31,25	31,20
La_2O_3	71,17	71,20	71,60	71,10
CO_2/La_2O_3	3,0	2,93	2,98	3,01

*Hydrogen was not detected in any of the forms; oxygen was determined by difference.

Table 2. Elemental Analysis of the Compound Brought to Constant Weight at 600° (suggested composition $La_2O_3 \cdot CO_2$)

Test Element*	Calculated, %	Found on precipit. from sol. of varying normality, %		
		1 N	0.1 N	0.01 N
C	3,35	3,23	3,30	3,13
O	21,60	22,97	23,80	21,07
La_2O_3	88,00	86,6	85,5	88,0
CO_2/La_2O_3	1,0	1,02	1,05	0,96

*Hydrogen was not detected in any of the forms; oxygen was determined by difference.

It is clear that the results of chemical analysis confirm the thermogravimetric results – the composition of the precipitates at 575° corresponds to the formula for the anhydrous carbonate with reasonable accuracy for all concentrations of the initial solutions used. The thermal decomposition product of the carbonate, which is stable over the range 550-675°, corresponds to the approximate formula $La_2O_3 \cdot CO_2$. Since the low temperature gravimetric forms of the rare earths are usually more readily soluble in acids than the oxides calcined at high temperatures, this compound, which, moreover, has a slightly higher weight – and, accordingly, a better conversion factor – can be recommended as a gravimetric form for the determination of lanthanum (precipitation with ammonium carbonate and calcination at 600°). The anhydrous carbonate is less suitable as a gravimetric form, both on account of its smaller thermal stability range, and because of a lower experimental accuracy (according to the thermogravigrams the deviations from the theroretical composition for the anyhdrous carbonate is 3-5%, while for the intermediate compound they do not exceed 1%).

SUMMARY

Formation of the normal carbonate of lanthanum $La_2(CO_3)_3 \cdot nH_2O$ has been thermogravimetrically confirmed in the system $LaCl_3 - Me_2CO_3$ ($Me = K^+, NH_4^+$) $- H_2O$. Thermal dissociation of this compound proceeds stepwise: $La_2(CO_3)_3 \cdot nH_2O \rightarrow La_2(CO_3)_3 \rightarrow La_2O_3 \cdot CO_2 \rightarrow La_2O_3$.

The thermal stability ranges of $La_2(CO_3)_3$ (300-400°) and $La_2O_3 \cdot CO_2$ (550-675°) have been determined.

The compound $La_2O_3 \cdot CO_2$ is recommended as a gravimetric form for the determination of lanthanum. Ammonium carbonate is the most suitable precipitant, while the calcination temperature is 600°.

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PHOTOMETRIC DETERMINATION OF GALLIUM WITH BUTYLRHODAMINE B

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Color reactions of $GaCl_4^-$ anions with the cation of basic organic dyes have acquired exceptional importance for the determination of microgram amounts of gallium; of these dyes the one which has found widest application is rhodamine B (or C) [1-6].

Rhodamine B contains an organic cation of large size. The presence of a carboxyl group in the rhodamine B molecule weakens to some extent the basic properties of this cation, and increases the solubility of the salts formed by rhodamine B.

Kuznetsov and Bol'shakova [7] have shown that completeness of precipitation, coprecipitation, and extraction of the elements can be appreciably increased if, instead of rhodamine B, one of its esters, e.g., the butyl ester of rhodamine B, so-called butylrhodamine B is used.

We have adopted butylrhodamine B for the photometric determination of gallium.

EXPERIMENTAL

The following reagents were used:

1. A 0.1% solution of butylrhodamine B in 6 N hydrochloric acid. The reagent was synthesized by Kuznetsov and Bol'shakova's method [7].

2. Gallium solution containing 1 mg gallium per ml of 6 N hydrochloric acid. The solution was prepared by dissolving an accurately weighed aliquot of spectrographically pure gallium metal in aqua regia; nitric acid was removed by a double evaporation with concentrated hydrochloric acid. The dry residue was dissolved in 6 N HCl. Working solutions of gallium containing 10, 1.0, 0.1 μg of gallium per ml were prepared by diluting the stock solution with 6 N HCl.

3. A 20% solution of titanium trichloride in 6 N HCl. The solution was prepared by dissolving titanium metal in hydrochloric acid.

The optical density was measured on a SF-4 spectrophotometer and on a FÉK-N photocolorimeter-nephelometer.

Butylrhodamine B is a dark-raspberry, crystalline material which is soluble in water, ethanol, and acetone; it is insoluble in benzene and toluene. A hydrochloric acid solution of butylrhodamine B has an orange-red color. Butylrhodamine B is hardly extracted at all from aqueous solutions by benzene, toluene, and chloroform.

In hydrochloric acid solution butylrhodamine B interacts with gallium to form a compound which can be extracted with benzene, and toluene, the extract obtained being rose-violet in color.

A toluene solution of butylrhodamine B chlorogallate has an absorption maximum at 565 mμ; at this wavelength the reagent itself hardly absorbs any light (Fig. 1).

One of the drawbacks of the rhodamine photometric determination of gallium by Onishi's method is the comparatively low extent to which the rhodamine B chlorogallate is extracted with benzene. Several authors have tried to improve Onishi's rhodamine method, and have recommended substitution of benzene by a mixture of benzene and ether [4], a mixture of chlorobenzene and CCl_4 [3], or a mixture of benzene and butyl acetate [5].

Butylrhodamine B is equally well extracted by benzene, toluene, and the mixed extractants mentioned above, so that there is no need to use the mixtures (Table 1).

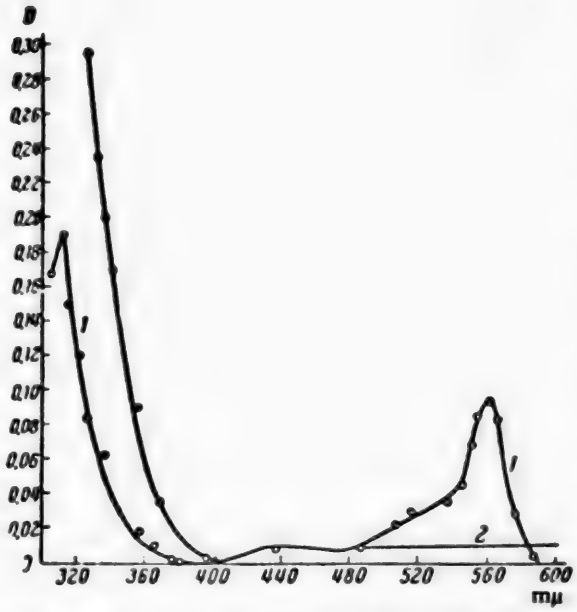

Fig. 1. Absorption curves. 1) Toluene extract of butylrhodamine B chlorogallate; 2) toluene extract of butylrhodamine B.

Table 1. Extraction of Butylrhodamine B Chlorogallate with Various Solvents

Solvent	Optical density		
	Blank	Test containing 0.4 μg Ga/ml	Difference
Benzene	0.009	0.410	0.401
Toluene	0.01	0.420	0.410
Benzene + ether (10 : 1)	0.013	0.425	0.412
Benzene + amyl acetate (4 : 1)	0.015	0.430	0.415

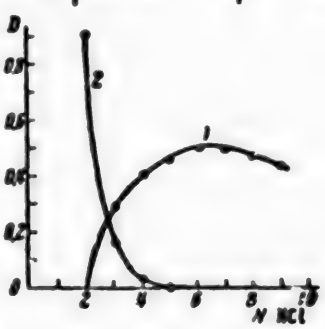

Fig. 2. Effect of hydrochloric acid concentration on extraction: 1) Butylrhodamine B chlorogallate with toluene (reference solution, the blank solution); 2) butylrhodamine B with toluene (reference solution, toluene.

A single extraction is sufficient to ensure almost complete extraction of butylrhodamine B chlorogallate by the solvents mentioned.

The sensitivity of the reaction of gallium with butylrhodamine B is almost one order higher than the reaction with rhodamine B. The limit of identification is 0.005 μg gallium in 1 ml of solution.

The molar extinction coefficient of butylrhodamine B chlorogallate is 90,000, while the molar extinction coefficient of rhodamine B chlorogallate determined by Onischi and Sandell [2] is 60,000.

Extraction of butylrhodamine B chlorogallate with toluene (benzene) depends on the acidity of the solution; the optimum acidity lies within the range 6 to 6.5 N HCl (Fig. 2).

It is interesting to note that extraction of the reagent itself becomes appreciable at low acidities of the solution, but there is hardly any extraction starting from 5 N HCl.

Colored solutions of butylrhodamine B chlorogallate conform to Beer's law over a wide gallium concentration range (0.005-2 μg/ml). Fig. 3 shows a calibration curve for a narrow concentration range (0.1-1 μg Ga in 1 ml of solution). The optical density was measured both on a spectrophotometer at 565 mμ, and also on a FÉK-N apparatus fitted with a 6-M filter, having maximum light transmission at 584 mμ; a 1 cm cell was used. Reference solutions were prepared by shaking hydrochloric acid solutions containing the same amounts of butylrhodamine B and titanium trichloride with toluene.

The elements which interfere with the determination of gallium by means of buytlrhodamine B are those elements which also interfere with determination of gallium with rhodamine B, i.e. Au^{III}, Fe^{III}, Sb^{V}, and Tl^{III}. The influence of these cations can be eliminated by adding titanium trichloride as a reducing agent to the test solution. In those cases where commercial hydrochloric acid, which usually contains traces of iron, is used, titanium trichloride must be added even when working with pure gallium solutions because of the high sensitivity of the reaction of butylrhodamine B with ferric iron (rhodamine B is less sensitive to iron).

Where test materials contain large amounts of aluminum (> 0.3 mg) gallium must be separated beforehand from aluminum. Extraction of gallium from 6 N HCl with ether, butyl or amyl acetate can be used for this purpose.

When test materials contain high contents of interfering elements it is always better to carry out a preliminary extraction of gallium in order to get reliable results.

Table 2. Determination of Gallium in Standard Samples

Samples	Ga%	
	Present	Found
Copper-zinc ore	0.0012	0.0012
Unroasted lead dust	0.0001	0.00009
Bauxite No. 1	0.0065	0.0069
Bauxite No. 2	0.0044	0.0042
Quartz-topaz greisens:		
No. 1	0.0020	0.0021
No. 2	0.0005	0.0005
No. 3	0.0003	0.00035

Gallium was determined by means of butylrhodamine B in a large number of different gallium-containing materials: unroasted lead dust, bauxities, copper-zinc ores, and quartz-topaz greisens.

Analytical Procedure. An aliquot of test material weighing from 0.1 to 0.5 g (depending on the gallium content) is fused in a corundum crucible with 1-1.5 g of Na_2O_2 and 0.5 g of NaOH at 600-650°. The melt is leached with hot water, the precipitate of hydroxides is dissolved in hydrochloric acid and the hydrochloric solution evaporated on a water bath until the dry salts are obtained. The salts are dissolved in 6 N hydrochloric acid and the solution transferred to a separating funnel.

Gallium is extracted three times with amyl acetate in the presence of a reducing agent – titanium trichloride; the funnel is shaken for 1.5-2 min each time.

The extract is washed three times with 6N HCl and the gallium reextracted three times with water. The aqueous solutions obtained are evaporated on a water bath until the dry salts are obtained, the latter are dissolved in 5 ml of 6 N HCl and transferred to a 25 ml separating funnel; the porcelain base used for the evaporation is rinsed with 2 ml of 6 N HCl. Two ml of 20% titanium trichloride solution is added to the separating funnel, the latter is shaken and 1 ml of 0.1% butylrhodamine solution added. Butylrhodamine B chlorogallate is then extracted with 10 ml of toluene (benzene) by shaking for 2 min. After the phases have separated out the aqueous solution is drained off, while the extract is filtered through a plug of glass wool to free it from drops of water; the first portion of filtrate is rejected, while the remainder is collected in a 1 cm cell.

The optical density is measured on a SF-4 spectrophotometer at 565 mμ or on a FÉK-N apparatus.

The amount of gallium is determined from the calibration curve.

Results for the determination of gallium in different materials are given in Table 2.

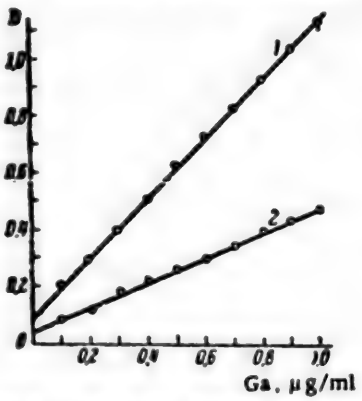

Fig. 3. Calibration lines for determination of gallium with butylrhodamine B on: 1) SF-4 spectrophotometer at 565 mμ; 2) FÉK-N photocolorimeter – nephelometer.

SUMMARY

The formation of a complex between $GaCl_4^-$ anions and butylrhodamine B, and the extraction of this complex (butylrhodamine B chlorogallate) with toluene (benzene) have been studied. It has been shown that this reaction is significantly more sensitive than the well known reaction with rhodamine B.

A method has been developed for the photometric determination of gallium with butylrhodamine B in various gallium-containing materials.

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PHOTOMETRIC DETERMINATION OF TITANIUM WITH 2-(α-N-PIPERIDINO) ISOPROPYL-4-HYDROXYTETRAHYDROFURAN-3-ONE

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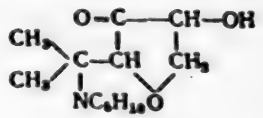
In acid media quadri . titanium forms soluble colored compounds [1] with certain substituted tetrahydrofuranones prepared in recen. ,ears by Nazarov et al [2].

We thought that it would be interesting to study the interaction of quadrivalent titanium ions with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one as a representative of the substituted tetrahydrofuranones, with the idea of establishing the possibility of using it for the determination of titanium.

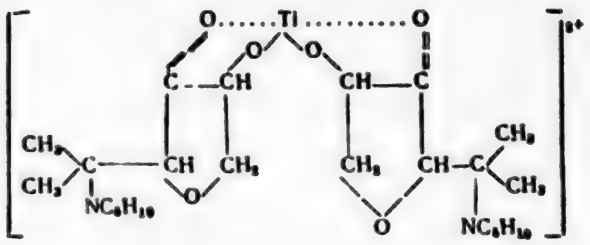


In acid solution (pH < 2) quadrivalent titanium forms with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one a soluble compound with an intense red-brown color, which is not destroyed in strong acids and in the presence of sulfates, oxalates, phosphates, borates, and other anions. In strongly acid media the solution of the titanium compound acquires a red-violet and even a blue color. The reaction is best carried out in a solution in which the hydrogen ion concentration is approximately equal to 1 g-equiv/liter. Using this reagent in acid solutions, titanium can be detected in the presence of all Group I-V cations, and in the presence of a number of rare metal ions: Li^{+}, Be^{2+}, Zr^{IV}, Ce^{IV}, VO_3^{-}. The sensitivity of detection is characterized by a limiting dilution of 1 : 1, 000, 000. The compound formed is fairly stable. The red-brown color obtained on adding a saturated aqueous solution of the reagent is preserved without change for 20 min after mixing the solutions; the red-brown colored compound formed when an alcoholic solution of the reagent is used is more stable; the optical density does not change over a one hour period.

The maximum absorption of solutions of the compound formed lies in the 420 mμ region (Fig. 1).

The molar ration which obtains during the interaction of quadrivalent titanium with the raegent was determined by the isomolar series method and by the equilibrium shift method [3, 4]. Several isomolar series were prepared which differed in their total concentration of reactants, the hydrogen ion concentration being constant for a particular series. The optical density was measured on a FÉK-M photoelectriccolorimeter using a path length of 1.035. The titanium and reagent concentration was varied over the range 0.00398-0.038 M, while that of the acid was varied between 0.04-1.9 g-equiv/liter. As the results obtained show (Fig. 2), the optical density is a maximum when the ratio of the components Ti : R = 1 : 2. The same ratio was obtained on using the equilibrium shift method, in which the optical density of solutions with a constant concentration of titanium and variable concentrations of the reagent was measured, the reagent concentration being varied over a wide range.

By means of electrophoresis (voltage 60-70 v) and ion exchange resins (sulfocoal in the H-form, and the resin ÉDÉ-10 in the OH-form) it was established that the titanium in the colored compound is found in the form of a cation. It should be pointed out that a complex with a ratio Ti : R = 1 : 2 is formed in acid solutions, in which, as is known [1], the reagent exists as the keto-form. Taking all this into account, the following probable structure can be advanced for the compound formed:



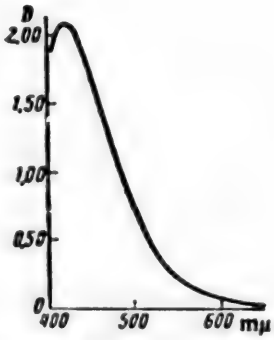


Fig. 1. Absorption spectrum of solutions of the compound of quadrivalent titanium with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one. SF-2M spectrophotograph. Titanium concentration 0.00045 M. Path length 5 mm.

Dilute solutions of the titanium compound formed (concentration 0.0020 M and lower) conform to Beer's law.

We have used the formation of a colored, soluble compound of titanium with 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one as the basis of a photometric method of determining titanium. As indicated above, none of the cations of Groups I – V, nor some rare metals, interfere with the qualitative detection of titanium.

Large amounts of trivalent iron interfere with titanium determination by increasing the color intensity of the solution. Nevertheless a tenfold excess of iron with respect to titanium does not interfere with determination of the latter. (Table 1).

Nickel and cobalt, even when present in large amounts, do not interfere with titanium determination (the original solution is used as the reference solution).

Sodium ethylenediaminetetracetate (EDTA-Na) does not affect formation of the compound of quadrivalent titanium with the reagent, and does not interfere with titanium determination.

Titanium Determination. The material whose titanium content is to be determined is dissolved in about 2 N sulfuric acid (where necessary it is fused with $KHSO_4$ and then dissolved), the amount taken being such that a solution with a titanium concentration not greater than 0.0020 M is obtained. 5-6 drops of a saturated alcoholic solution of the reagent is added to 5 ml of the solution obtained, and the optical density measured using a green filter. The titanium content of the sample is determined from a calibration curve (constructed beforehand). The optical density can be measured within one hour of mixing the solutions. The original solution of test material is used as the reference solution.

When large amounts of iron are present, the titanium must be separated. Titanium does not form a stable complex with EDTA-Na [5]. Titanium is precipitated from solution with ammonia after addition of EDTA-Na, the precipitate is dissolved in sulfuric acid and the titanium determined as described above.

Results for the determination of titanium in several alloys ("standard samples") and minerals are given in Table 2.

TABLE 1. Effect of Accompanying Elements on the Optical Density of Solutions of the Titanium Compound

Titanium content, mg/liter	Impurity, g/liter			Optical density, λ=530mμ	Titanium content, mg/liter	Impurity, g/liter			Optical density λ=530mμ
	Fe^{III}	Co^{II}	Ni^{II}			Fe^{III}	Co^{II}	Ni^{II}	
42,6	—	—	—	0,21	85,3	—	18,4	—	0,37
42,6	0,45	—	—	0,21	85,3	—	27,6	—	0,37
42,6	0,89	—	—	0,23	85,3	—	55,2	—	0,38
42,6	1,34	—	—	0,24	85,3	—	—	56,2	0,37
85,3	—	—	—	0,37	85,3	—	—	84,2	0,37

Table 2. Determination of Titanium in Samples

Test Sample	Titanium content	Titanium found	Error, %
	%	%	
Instrument steel (EI 184)	0.01	0.0098	2.0
Steel (EI 274)	0.06	0.059	1.5
Ferrotitanium	29.0	28.99	0.03
Ilmenorutile mineral	53.04	52.96	0.15

Thus titanium can be determined with a reasonable degree of accuracy in alloys and minerals by means of 2-(α-N-piperidino)isopropyl-4-hydroxytetrahydrofuran-3-one.

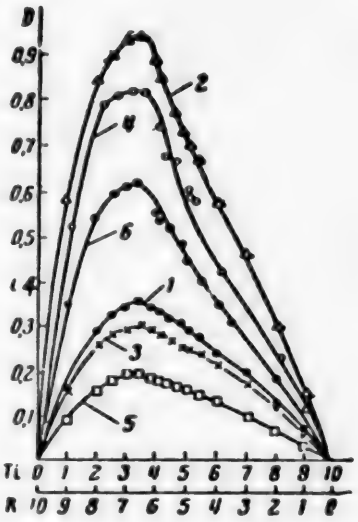


Fig. 2. Isomolar series in the system Ti^{IV} – 2-(α-N-piperidion) isopropyl-4-hydroxytetrahydrofuran-3-one. 1,2) 7.96×10^{-3} M titanium and reagent, 0.16 g-equiv H^+ per liter; 3,4) 7.96×10^{-3} M titanium and reagent, 0.5 g-equiv H^+/liter; 5, 6) 3.98×10^{-3} M titanium and reagent, 0.16 g-equiv H^+/liter (1, 3, 5 at 530 mμ; 2, 4 6 at 400 mμ).

SUMMARY

Quadrivalent titanium ions interact with 2-(α-N-piperidino) isopropyl-4-tetrahydrofuran-3-one to form a soluble compound with a red-brown color. The maximum absorption of solutions of the compound formed lies at 420 mμ; solutions of the complex conform to Beer's law.

A photometric method has been developed for the determination of titanium by means of 2-(α-N-piperidino) isopropyl-4-hydroxytetrahydrofuran-3-one.

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AMPEROMETRIC TITRATION OF GERMANIUM WITH A SOLUTION OF PYROCATECHOL

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Determination of large amounts of germanium is carried out mainly by chemical methods at present. The most widely used of these methods is the gravimetric one based on precipitation of germanium with hydrogen sulfide, followed by conversion of the sulfide into the oxide [1]. The titrimetric method consists in titrating germanic acid with alkali in the presence of mannitol or glucose. When this method is used, germanium is separated from other elements by distillation as germanium chloride or by precipitation with hydrogen sulfide [2, 3].

We have developed a method for the amperometric titration of germanium with a pyrocatechol, using a dropping mercury electrode in an electrolyzer provided with an external anode.

The reference electrode was a saturated calomel electrode which was connected to the electrolyzer via an agar-agar bridge.

Titration was carried out with a 0.1 M solution of pyrocatechol measured out from a microburet with 0.01 mm scale division. A borate-acetate buffer with a pH 7-9 (0.2 M CH_3COONa + 0.05 M $Na_2B_4O_7$) proved to be the most suitable supporting electrolyte for titration. In contrast to the acetate supporting electrolyte we described earlier [4], the borate-acetate buffer permits one to obtain a clearly defined germanium wave at high concentrations of the latter in solution (8-10 mM/liter). Under these conditions a linear relation is observed between germanium concentration and its wave height. The half-wave potential of germanium under these conditions is −1.45 to −1.47 v; the limiting current can be measured at potentials of −1.6 to −1.8 v.

We established that addition of pyrocatechol leads to a decrease, and when a small excess has been added, to the disappearance of the germanium wave. Pyrocatechol itself, over the pH range in which germanium is polarographed, does not give a wave (Figs. 1 and 2).

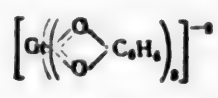
Titration of solutions with different germanium concentrations at −1.7 v showed that the molar ratio of pyrocatechol and germanium is constant as long as the germanium concentration of the solution being titrated is not less than 4mM/liter.

TABLE 1

Germanium concentration, mM/liter	No. of moles of pyrocatechol per mole of germanium
0.1	26.5
0.2	20.0
1	5.0
2	4.1
3	3.7
4	2.9
6	3.1
8	3.0

When this condition is observed three moles of pyrocatechol interact with one mole of germanium; this might possibly indicate formation of a complex with a coordination number of p = 3.

On the basis of these experimental results, and by analogy with the known pyrocatechol complexes of Si, Ti, Fe, etc [5-7], it may be postulated that the following complex ion is present in solution:



The absence of a germanium wave in the presence of excess pyrocatechol, i.e. the wave is shifted by not less than −0.5 v, indicates that the complex formed possesses high stability.

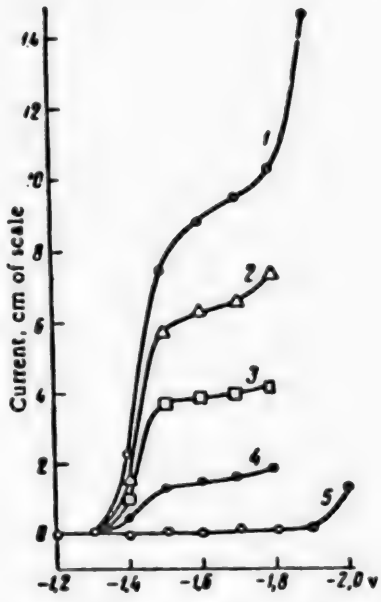


Fig. 1. Germanium polarograms (0.06 mM in 10 ml) in a supporting electrolyte of 0.2 M CH_3COONa + 0.05 M $Na_2B_4O_7$ for the following pyrocatechol contents: 1) 0; 2) 0.05 mM; 3) 0.10 MM; 4) 0.15 mM 5) 0.2 mM; S = 1/50.

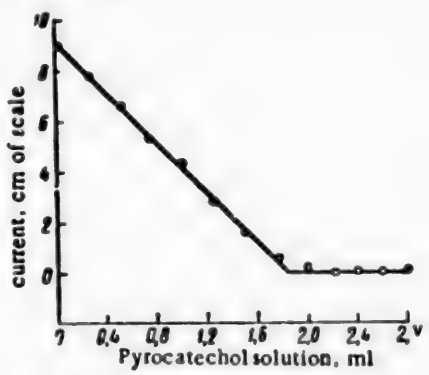


Fig. 2. Titration curve of germanium (6 mM/liter) with 0.1 M pyrocatechol solution in a borate-acetate supporting electrolyte. Initial volume of solution 10 ml; S = 1/50.

Titration of a solution with a germanium content of 5 mM/liter at different pH values showed that on increasing the pH from 6.8 to 9.1 the height of the germanium wave decreases by one third while the amount of pyrocatechol used up in a titration decreases by only 2.6%. Accordingly, at high germanium contents amperometric titration gives more reliable results than the polarographic method.

Pyrocatechol interacts with many elements; accordingly, during determination of germanium in complex materials, germanium must be removed beforehand. This was accomplished by the generally adopted method of extracting with carbon tetrachloride [8].

Germanium can be separated from all elements apart from arsenic by this method. Arsenic in its trivalent form distorts the germanium wave during titration with pyrocatechol. Quinquevalent arsenic, however, does not affect reduction of germanium on the dropping mercury electrode. Accordingly, after extraction of germanium, it is recommended that trivalent arsenic be reduced to its quinquevalent state by means of iodine in the presence of starch.

Germanium is determined as follows. An aliquot of test material (2-4 g for germanium contents up to 1%, 0.2-1 g for germanium contents greater than 1%) is decomposed by the usual method with a mixture of acids, or by fusion with sodium peroxide [9-10]. When the second technique is used, after the melt has been leached it is essential to add hydroxylamine to destroy the hydrogen peroxide.

The test solution, whose volume amounts to 15-30 ml, is transferred to a separating funnel, and concentrated hydrochloric acid in an amount equal to three times the volume of test solution is added, followed by 50 ml of carbon tetrachloride. The mixture to be extracted is then cooled in order to avoid volatilization of germanium, which occurs at elevated temperatures, and extraction is carried out for 2 min. Forty ml of carbon tetrachloride is used for the second extraction; after this extraction the organic layer is washed with 10 ml of 10 N hydrochloric acid.

The germanium is reextracted from the combined extracts with two portions of water, the first of 10 ml and the second of 5 ml. The aqueous solution containing the germanium is transferred to a 25 ml standard flask, the pH is adjusted to eight with the buffer solution (4 M CH_3COONa and 0.1 M $Na_2B_4O_7$), and if necessary with a few drops of 1 N sodium hydroxide, using ZIV-1 or phenolphthalein as indicator. Trivalent arsenic is then oxidized with 0.01 N iodine solution in the presence of two drops of 1% starch solution, and the volume finally made up to the mark with buffer solution.

Ten ml of this solution is transferred to the electrolyzer, and after purging for 5 min with hydrogen, it is titrated at − 1.7 v with 0.1 M pyrocatechol solution delivered from a microburet.

The pyrocatechol solution is standarized amperometrically with a standard germanium solution, using the same supporting electrolyte.

The method which we recommended was checked on samples containing appreciable amounts of copper, zinc, lead, arsenic, and other elements.

Results of amperometric, polarographic, and photometric determinations are compared in Table 2.

This method was also tested on samples to which a standard germanium solution was added.

TABLE 2

Germanium found, %		
Amperometrically	Polarographically	Photometrically
0.25	0.29	–
0.25	0.24	–
0.20	0.22	0.20
0.18	0.21	0.18
0.24	0.24	
0.35	0.34	0.37
2.79	0.79	2.86

TABLE 3

Germanium				
Amount in test sample, mg	Added, mg	Total taken, mg	Found, mg	Error (relative), %
8.8	7.3	16.1	15.9	1.24
9.5	3.6	13.1	12.7	3.06
1.7	7.3	9.0	8.4	3.67
0.34	7.26	7.6	7.2	5.2

The experimental results are shown in Table 3; it is clear from these results that the mean error is 4.1%.

The method developed can therefore be recommended for the determination of germanium at the level of tenths of a percent and whole percentages.

SUMMARY

A new method has been developed for the amperometric titration of germanium with a pyrocatechol solution; the supporting electrolyte consists of sodium acetate and sodium tetraborate at pH 7-9, while a dropping mercury electrode is used as the indicator electrode.

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AMPEROMETRIC TITRATION OF THORIUM SALTS WITH CUPFERRON

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Cupferron has found wide application in chemical analysis for the gravimetric determination of a number of elements. In amperometric titration use is made of the property of cupferron to be reduced on a dropping mercury electrode, and also to be oxidized on a rotating platinum electrode during determination of titanium [1-4], zirconium [5-7], and some rare earths [11]. The composition of the cupferronates of the rare earths of the cerium group which are formed corresponds to the formula $MeCup_3$ [8-11], while that for the cupferronates of the yttrium group of the rare earths corresponds to $MeCup_3$ and NH_4Cup [12].

Thorium also forms sparingly soluble cupferronates; published information on the conditions under which they are formed is, however, contradictory. In all the methods described, it is recommended that the final state in the determination should be calcination to the oxide. Thornton [13] has indicated that it should be possible to precipitate thorium with cupferron from acetic acid solutions not containing free sulfuric acid. Lendell et al [14] recommend that precipitation should be carried out at pH 4 and higher, but also refer to the possibility of precipitating thorium even from very concentrated hydrochloric acid solutions. Eckhert and Bane [15] indicate that thorium forms several complex compounds with cupferron, and that a precipitate is formed on adding cupferron to sulfuric acid solutions of thorium at pH 3.5-4.5.

The aim of the work described here was to establish more accurately the conditions leading to the formation of thorium cupferronate, to determine the composition of the precipitate, to study the effect of foreign ions, and to establish the possibility of titrating thorium amperometrically with cupferron in the presence of the rare earths.

10^{-2}M solutions of chemically pure thorium nitrate, and of the nitrates and chlorides of cerium, lanthanum, praseodymium, neodymium, and yttrium were used in the course of the work. The concentration of the solutions was determined gravimetrically: the oxalate method was used for thorium, and the hydroxyquinoline method for the rare earths.

Cupferron solutions were prepared by the method described by Kul'berg [16] and by Usatenko and Bekleshova [2-3], both with and without the use of a stabilizer—phenacetin. The concentration of the cupferron solutions was determined by amperometric titration of titanium sulfate solutions [2-3]. Citric and sulfosalicylic acids were used as 0.5 M solutions.

The ammonia-acetate buffer solutions were prepared from chemically pure grade reagents. pH was controlled potentiometrically. The remaining reagents were used in the form of their 0.1-0.2 M solutions, while coagulators were used in the form of the chemically pure dry salts.

Titration was carried out with a rotating platinum anode (l = 8 mm, d = 0.5 mm) and a saturated calomel electrode, at an applied potential of 1.0 v. The diffusion current was recorded with a type ϕ galvanometer on a scale with 100 divisions, one whole division being equal to 0.42×10^{-9} amp. Five ml of buffer solution was used when the total volume of solution being titrated was 10-15 ml.

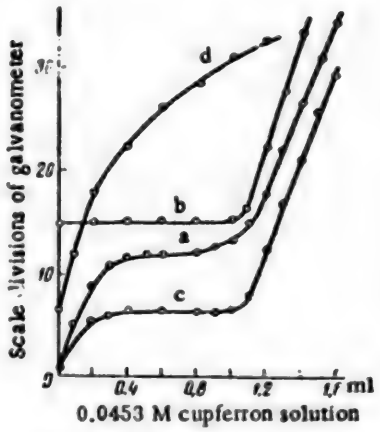
Investigation showed that the most reproducible results for titration of thorium are obtained at ph 3-4. Appreciable formation of a precipitate is observed on addition of approximately 1/4-1/3 of the volume of precipitant corresponding to the equivalence point (fig., a). We originally interpreted this as formation of a complex ion with the composition $ThCup^{3+}$. However, on measuring the value of the diffusion current of solutions containing increasing amounts of equimolar mixtures of thorium nitrate and cupferron, no increase in i_d was observed. Obviously, the first increase in i_d on the titration curve (fig., a) is determined not by formation of a complex ion and its oxidation on the anode, but by the appreciable solubility of the precipitate. The precipitate tends to form a colloid. In order to prevent colloid formation, and to lower the solubility, we tested some electrolyte-coagulators – the chlorides, nitrates,

Table 1 Titration of a Thorium Salt Solution with Cupferron (Total volume 10 ml; pH 4.2; 3 g NaCl).

Thorium M x 10^{-5} taken	M x 10^{-5} cupferron taken for titration	Mean M x 10^{-5} cupferron	M_{Cup}/M_{Th}
0,12	0,47; 0,50; 0,49; 0,50; 0,48;	0,49	4,08
0,24	0,99; 1,00; 0,97; 0,97; 0,88	0,98	4,08
0,48	1,95; 1,90; 1,92; 1,94; 1,93	1,93	4,02
1,20	4,75; 4,70; 4,72; 4,80; 4,73	4,70	3,92
2,80	11,18; 11,12; 11,18; 11,12; 11,15	11,15	3,98
5,60	22,40; 22,60; 22,47; 22,50; 22,54	22,50	4,02

Table 2 Titration of Cupferron Solution with a Thorium Salt (Titration conditions the same as given in Table 1).

M x 10^{-5} cupferron taken	M x 10^{-5} M thorium nitrate solution taken for	Mean	M_{Cup}/M_{Th}
0,50	0,12; 0,13; 0,15; 0,10; 0,15	0,13	3,85
2,00	0,55; 0,45; 0,45; 0,50; 0,45	0,48	4,16
10,00	2,49; 2,52; 2,49; 2,49; 2,50	2,50	4,00
20,00	5,10; 4,96; 4,98; 4,98; 5,08	5,02	3,98



Titration curves of 1.2×10^{-5} M thorium nitrate with 0.0453 M cupferron solution. Volume 10 ml, pH 4.1. a) Without a coagulator; b) with a coagulator, 0.05 mole NaCl; c) in the presence of 0.05 mole $NaNO_3$; d) in the presence of 0.025 mole Na_2SO_4.

and sulfates of the alkali metals and ammonium. In the presence of sulfates, titration of thorium with cupferron is impossible; apparently, the sulfate complex of thorium is more stable than its cupferronate (fig., d). The chlorides proved to be most effective, the best of these being sodium chloride when the amount of it present in 10-15 ml of solution being titrated was 3-5 g (fig., b). Under these conditions a precipitate is formed on adding the first drops of precipitant.

As the results in Tables 1 and 2 show, at the equivalence point the molar ratio of cupferron to thorium is equal to 4:1, both during direct and back titration; this confirms formation of a precipitate with the composition $ThCup_4$. Formation of a precipitate occurs in the course of the first 45-60 sec, accordingly, during titration the current was measured one minute after adding fresh portions of precipitant.

At pH 4 and higher, the rare earths, like thorium, are titrated with cupferron to form precipitates with the composition $MeCup_3$ [11]. As shown below, in the presence of appropriate masking agents, and also on lowering the pH of the solutions below 4, it is possible to carry out selective titration of thorium with cupferron in the presence of the rare earths. The limiting ratio of Th: rare earth for which satisfactory titration results are obtained depends on the pH of the solution and on the nature of the masking agent.

Citric and sulfosalicylic acids, which are used in the analysis of minerals containing thorium and the rare earths, were used as masking agents for the rare earths. Thus the use of citric acid in amounts not greater than 1.0-1.5 ml of 0.5 M solution in buffered solutions with pH 3, when the total volume is 10 ml, makes it possible to determine thorium in the presence of equimolar amounts of the rare earths with reasonable accuracy. However, if the same volume of citric acid is used in solutions not containing buffer mixtures (the pH being equal to 2.0-2.5), then it is possible to determine thorium at molar ratios to the rare earths of 1:2 and even 1:2.5. The relative error does not exceed 3. Increasing the citric acid concentration leads to partial dissolution

Table 3. Determination of Thorium and Total Rare Earths by Amperometric Titration with Cupferron Solution*

Thorium, mg		Mean deviation of an individual determination		Probable deviation of an individual determin.		Rare earths introduced into the mixture, mg	Found in the mixture**	Mean deviation of an individual determination		Probable deviation of an individual determination	
Taken	Found**	Absolute	Relative	Absolute	Relative			Absolute	Relative	Absolute	Relative
0,602	0,606	0,012	2,06	0,011	1,81	1,200	1,244	0,034	2,78	0,031	1,50
0,602	0,606	0,010	1,65	0,008	1,32	2,543	2,600	0,023	0,88	0,020	0,77
0,602	0,615	0,011	1,79	0,010	1,62	2,907	2,948	0,62	2,10	0,050	1,70
2,408	2,394	0,037	1,55	0,030	1,26	4,800	4,906	0,116	2,36	0,096	1,97
6,020	6,035	0,112	1,85	0,098	1,61	25,430	25,969	0,418	1,49	0,320	1,23
6,020	5,816	0,110	1,96	0,090	1,60	29,070	29,408	0,508	1,75	0,432	1,47
8,190	8,364	0,199	2,38	0,174	2,08	16,313	16,216	0,071	0,44	0,041	0,25
8,190	8,368	0,176	2,10	0,167	2,00	39,532	40,243	0,704	1,75	0,564	1,40

*Total Th and rare earths was titrated at pH 4.2 in a volume of 10-15 ml.

**Arithmetic mean of 5 determinations.

of the cupferronate, while an increase in the amount of rare earths leads to their coprecipitation with thorium.

Replacement of citric acid by its potassium salt leads to formation of double salts of the rare earths, as shown in [17], and to the formation of thorium precipitates of variable composition, in which the molar ratio of cupferron to thorium increases with increasing concentration of potassium citrate.

The use of sulfosalicylic acid as a masking agent permits readily reproducible titration results to be obtained even at pH 1.7-1.5. Such an increase in acidity does not only increase the solubility of the cupferronates of the rare earths, but also favors increasing adsorption of foreign ions by the thorium cupferronate precipitate. The optimum sulfosalicylic acid content during titration is 0.1-0.15 M (2-3 ml of 0.5 M acid in 10 ml of the solution being titrated). At higher sulfosalicylic acid concentrations dissolution of the thorium cupferronate precipitate is observed and the titration results obtained are low.

Prolonged storage of solutions (30-48 hr) containing thorium cupferronate, sodium chloride, sulfosalicylic acid, and a small excess of cupferron is accompanied by partial and sometimes complete dissolution of the precipitate.

Under the conditions used for titrating thorium, in the presence of sulfosalicylic acid at pH 1.5 (2 ml of 0.5 M HSal*, 3 g NaCl, volume 10 ml), trivalent ions of the rare earths of the cerium and yttrium groups are not precipitated by cupferron. Satisfactory results for thorium are obtained when the molar ratios of thorium to lanthanum, praseodymium, neodymium, and yttrium in mixtures are less than or equal to 1:8:10:10:8 respectively. The exception is trivalent cerium, in the presence of which satisfactory results are obtained when the ratio is Th:Ce = 1:2.5. When, in addition to cerium, other representatives of the rare earths tested are present, cerium has hardly any effect.

Salts of the alkaline earth metals do not interfere with titration at ratios of Th:Ca:Mg etc. of the order of 1:500-800; aluminum and beryllium do not interfere at ratios of 1:400. Phosphates and silicates do not interfere with titration. Trivalent iron, zirconium, and titanium are coprecipitated with thorium, and interfere with titration. Fluorides, sulfates, and sodium ethylenediaminetetracetate interfere with titration.

On the basis of the work carried out, the following method can be recommended for the determination of thorium and total rare earths in mixtures of their salts.

An aliquot of test solution containing from 0.2 to 5-10 mg of thorium and a corresponding amount of the rare earths is transferred to a 50 ml beaker; 3 g of NaCl and 5 ml of buffer solution with pH 5 ± 0.2 are added, and the volume of the solution made up to 10 ml with distilled water (the final pH should be 4-4.5). A rotating platinum electrode is immersed in the solution, as well as the bridge connecting the saturated calomel electrode; a potential of 1 v is applied (with respect to the saturated calomel electrode) and the solution titrated with cupferron solution, the galvanometer readings being taken one minute after each new portion of precipitant is added. Under these conditions, thorium and total rare earths are titrated.

*Sal represents the anion of sulfosalicylic acid.

To a second aliquot of the same solution is added 3 g NaCl and 2 Ml of 0.5 M sulfosalicylic acid; the volume is made up to 10 ml with water, and the solution titrated. The volume of cupferron solution used in this case corresponds to the thorium content.

For thorium contents of less than 2.0 mg it is recommended that titration be carried out with 0.01-0.02 M cupferron solution, while for thorium contents of 1-10 mg, titration is carried out with 0.05 M cupferron solution; at higher thorium concentrations, in the presence of large amounts of the rare earths, it is recommended that 0.07-0.1 M cupferron solutions be used for titrating.

Results for the determination of thorium and total rare earths given in Table 3 show that reasonably good reproducibility and accuracy are possible.

SUMMARY

Thorium forms a precipitate of composition $ThCup_4$ with cupferron over a wide pH range in the absence of strong acids and sulfates. The precipitate tends to form a colloid, and coagulators must be used; sodium chloride is the most efficient for this purpose.

Sulfosalicylic acid exhibits a stronger masking effect than citric acid during titration of thorium in the presence of the rare earths.

Optimum conditions have been established for the amperometric titration of thorium in the presence of cerium group rare earths. The method suggested has been checked on synthetic mixtures. The reproducibility and accuracy of the method are satisfactory.

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ANODE AMPEROMETRIC TITRATION OF BISMUTH ON THE BASIS OF THE FORMATION OF IODOBISMUTHITES

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We have shown previously that it is possible to carry out quantitative amperometric determination of bismuth on the basis of the formation of the iodobismuthites of 8-hydroxyquinoline [1] and pyramidone [2], and that amperometric titration can be carried out on the basis of both the cathode and anode current. In the first instance [1], bismuth is titrated with a dropping mercury electrode and with rotating platinum microelectrodes, while in the second instance bismuth can only be titrated with a dropping mercury electrode. On the basis of the fact that certain other organic bases are also capable of forming sparingly soluble compounds with potassium iodobismuthite [3-6] in acid media, we decided to investigate the possibility of using some of these bases for the quantitative determination of bismuth by an anode amperometric method on a setup provided with a rotating platinum microelectrode.

Table 1. Titration of Bismuth with Potassium Iodide in the Presence of 500 mg Antipyrine in a Supporting Electrolyte of 2.5 M Sulfuric Acid. Titration on the Basis of the Anode Current (mean of 4-5 determinations)

Bismuth, mg		Deviation of the mean found from that taken, %
Taken	Found	
43,80	43,58	0,52
32,85	32,68	0,51
20,98	20,99	0,04
10,49	10,62	1,15
5,25	5,83	11,04

Experiments on amperometric titration of bismuth with potassium iodide in the presence of organic bases were carried out as before [1], on the basis of the oxidation current of iodide ions at a platinum electrode potential of +0.44 v, and using a setup of the usual type provided with a rotating platinum microelectrode. At higher potentials the platinum electrode becomes covered with a black precipitate of iodine. By titrating on the basis of the anode current, interference from oxygen and a number of other readily reduced ions is avoided. A saturated calomel half-element with a large mercury surface was used as the nonpolarizing electrode. The electrolyte bridge which connected the solution being titrated with the calomel half-element through an intermediate vessel containing potassium chloride was filled with potassium nitrate solution. The current was measured with a mirror galvanometer fitted with a shunt. The platinum electrode, which was rotated at 700 rpm, was a glass tube 10 mm in diameter with a fused side arm close to the lower sealed end with a platinum wire 0.4 mm in diameter and 4 mm long. Titration was carried out in the usual 100 ml beakers. The potassium iodide solution was added from a tapless microburet of the Shilov type; the capacity of the buret was 5 ml, while the scale divisions were 0.02 ml. The platinum electrode was cleaned with concentrated nitric acid and rinsed with water before each titration.

The potassium iodide solution was prepared by dissolving an accurately weighed amount of the chemically pure salt in water, while the bismuth nitrate solution was prepared by dissolving an aliquot of chemically pure bismuth metal in nitric acid (1:1), followed by dilution to a definite volume with water. The amount of nitric acid taken was sufficient to dissolve the bismuth and to give a final solution with an acidity of 0.4 N.

Titration was carried out as follows. 0.5 g of the organic base was added to the bismuth nitrate solution contained in a beaker. The optimum acidity of the solution for carrying out titration of bismuth had been determined beforehand in special experiments; the requisite acidity was then obtained by adding a known amount of 18 N sulfuric acid and water. The volume of solution being titrated was 40 ml in all experiments. The requisite potential of the indicator electrode was applied and titration with potassium iodide carried out. The initial value of the current was recorded, and subsequently the current was recorded after addition of each portion of reagent; initially the reagent was added in large aliquots to the appearance of a large current, but toward the end the reagent was added in small amounts, 1-2 drops. The end point was established by the usual graphical method.

Table 2. Titration of 21.22 mg of Bismuth with Potassium Iodide in the Presence of Foreign Ions in a Supporting Electrolyte of 2.5 M Sulfuric Acid, at a Platinum Electrode Potential of +0.44 v, and in the Presence of Antipyrine (mean of 4-5 determinations)

Foreign salt	Molar ratio	Bismuth found, mg	Dev. of the mean found from that taken, %	Foreign salt	Molar ratio	Bismuth found, mg	Dev. of the mean found from that taken, %
KNO_3	100	20,95	1,27	$Pb(NO_3)_2$	1	21,14	0,38
KNO_3	50	21.21	0,05	$FeSO_4$	100	21,14	0,38
$KC_2H_3O_2$	200	21,16	0,27	$MnSO_4$	100	21,30	0,38
KCl	20	20,46	3,59	$CoSO_4$	50	21,10	0,55
KCl	10	21,10	0,55	$ZnSO_4$	50	21,18	0,18
KCl	5	21,22	0,00	$KAl(SO_4)_2$	100	21,26	0,18
(EDTA-Na)	100	21,06	0,73	$NiSO_4$	50	21,34	0,55
(EDTA-Na)	50	21,10	0,60	$MgSO_4$	100	21,33	0,50
Tartaric acid	200	21,37	0,69	$Cr_2(SO_4)_3$	50	21,33	0,50
Tartaric acid	100	21,26	0,19	$CdSO_4$	5	21,67	2.12
Na_2HPO_4	100	21,19	0,14	$CdSO_4$	2,5	21,14	0,38
Citric acid	50	21,38	0,75	Antimonyl potassium	1	21,26	0,18
Citric acid	100	21,42	0,93	tartrate			
$Pb(NO_3)_2$	25	20,05	5,57	Sodium arsenite	1	20,99	1,08

Titration of Bismuth with Potassium Iodide in the Presence of Antipyrine. During titration of equal amounts of bismuth (20.98 mg in 40 ml of solution) with potassium iodide in the presence of 500 mg antipyrine at a platinum electrode potential of +0.44 v, it was established that satisfactory results, close to the true values, are obtained when the acidity of the solution being titrated is 2.5 M. At lower acidities high results are obtained for bismuth, while at very high acidities the results are low, the results being lower the higher the acidity of the solution being titrated. Thus in the presence of antipyrine, as before in the presence of pyramidone [2], the optimum acidity of the solution being titrated is 2.5 M. The amount of antipyrine used during titration of bismuth with potassium iodide should be 20-40 times that of the bismuth.

As Table 1 shows, the results of titrating bismuth are completely satisfactory and are reasonably reproducible. There is a fairly good proportionality between the amount of potassium iodide used and the amount of bismuth: four iodide ions correspond to one bismuth ion.

It is clear from Table 2 that even very large amounts (100-200×) of nitrates, acetates, tartrates, citrates, sulfates, and phosphates, as well as sodium ethylenediaminetetracetate do not interfere with bismuth titration. Chloride ions at concentrations not greater than ten times that of bismuth do not interfere with titration of the latter. At higher concentrations chloride ions lower the results for the titration of bismuth, since, apparently, they partly enter into the composition of the bismuth complex instead of the iodide ions.

Many cations do not interfere either. Thus even very large (50-100 ×) amounts of divalent iron, manganese, zinc, aluminum, magnesium, cobalt, nickel, and chromium do not interfere during bismuth titration. Appreciable amounts of lead, cadmium, trivalent antimony, and arsenic interfere. Satisfactory results can be obtained for bismuth when the amount of lead, trivalent antimony, and arsenic is the same as that of bismuth (1:1). When cadmium is present, bismuth can only be titrated when the cadmium concentration is not more than three times that of bismuth.

The method developed has been checked on synthetic mixtures of chemically pure metals (58.14% Bi, 16.62% Cd, and 25.24% Pb). 2.0849 g of alloy was dissolved in 20 ml nitric acid (1:1), the solution was transferred to a 500 ml standard flask and its volume made up to the mark with water. An aliquot of this solution was titrated by the anode amperometric method with potassium iodide in the presence of antipyrine. The mean of five determinations of bismuth in the mixture deviated by 0.20% from the amount taken.

Titration of Bismuth with Potassium Iodide in the Presence of Pyramidone. It has been shown earlier that it is possible to titrate bismuth amperometrically with potassium iodide in the presence of pyramidone on a setup with a dropping mercury electrode [2]. Taking into account the advantages of a rotating solid microelectrode over a dropping mercury electrode, in the course of the work described here we studied the possibility of determining bismuth by an anode amperometric method using a rotating platinum microelectrode in the presence of pyramidone.

Table 3. Anode Titration of Bismuth with Potassium Iodide in the Presence of 500 mg Pyramidone in a Supporting Electrolyte of 2.5 M Sulfuric Acid (mean of 4-5 parallel determinations)

Bismuth, mg		Deviation of the mean value found from that taken%
Taken	Found	
43,80	43,97	0,39
32,85	32,66	0,57
31,47	31,53	0,19
20,98	20,90	0,38
10,95	10,62	3,01
5,25	5,60	6,66

Table 4. Anode Titration of Bismuth with Potassium Iodide in the Presence of 200 mg β - Naphthoquinone in a Supporting Electrolyte of 3.5 M Sulfuric Acid (mean of 5-6 parallel determinations)

Bismuth, mg		Deviation of the mean value found from that taken %
Taken	Found	
54,50	54,53	0,05
43,60	43,58	0,04
41,32	41,62	0,73
32,70	32,70	0,00
20,66	20,72	0,29
16,35	16,30	0,31
10,33	10,68	3,38

Experiments on the amperometric titration of equal amounts (20,98 mg in 40 ml) of bismuth with potassium iodide in the presence of pyramidone, at various acidities of the solution being titrated, showed that the best results are obtained at an acidity of 2.5 M, as during titration with a dropping mercury electrode. At lower acidities the results are high, while at higher acidities they are low.

It is clear from Table 3 that anode amperometric titration of bismuth in the presence of pyramidone gives fairly accurate and reproducible results during determination of various amounts of bismuth. Solutions containing small amounts of bismuth are not titrated so well because of the solubility of the precipitate.

We did not study the influence of foreign ions on the results of titrating bismuth in the presence of pyramidone in the work described here, since it has been studied earlier during titration of bismuth with a dropping mercury electrode [2]. Those anions and cations which do not interfere during titration in the presence of antipyrine and 8-hydroxyquinoline, should not interfere with titration of bismuth with potassium iodide (in the presence of pyramidone) by the anode amperometric method.

Titration of Bismuth with Potassium Iodide in the Presence of β-Naphthoquinoline. On the basis of the capacity of β-naphthoquinoline to precipitate bismuth from acid solutions in the presence of chloride, bromide, iodide, and thiocyanate ions, we thought it would be interesting to investigate the possibility of using it for determining bismuth by anode amperometric titration with potassium iodide.

Experiments on the titration of equal amounts of bismuth (20,66 mg) in 40 ml of solution showed that again in this case the results depend on the acidity of the solution being titrated. The best results, i.e. those nearest the true values, are obtained on titrating in a supporting electrolyte of 3.5 M sulfuric acid (Table 4). At lower acidities the results are high, while at higher acidities they are low. The amount of β-naphthoquinoline should not exceed the amount of bismuth in the solution being titrated by more than 30-40 times. In our experiments the amount varied from 75 to 300 mg. The presence of large amounts of β-naphthoquinoline leads to a slight increase in the results.

Presumably those anions and cations which do not interfere during titration in the presence of antipyrine, pyramidone, and 8-hydroxyquinoline, should not interfere during titration of bismuth by the given method in the presence of 8-naphthoquinoline.

Titration of Bismuth with Potassium Iodide in the Presence of Some Other Organic Bases (Cinchonine, Quinine, and Anabasine). Finally we established, in principle, the possibility of using cinchonine, quinine, and anabasine for the amperometric titration of bismuth with potassium iodide. During titration of strongly acid solutions of bismuth containing an excess of any one of the organic bases mentioned, the limiting current is established fairly rapidly after addition of each portion of reagent, while the titration curves obtained are very clearly defined and have an almost horizontal left hand branch and a simply rising right hand branch. The precipitates of cinchonine and quinine iodobismuthites formed during titration are reminiscent in character and color of the precipitates obtained in the presence of 8-hydroxyquinoline, pyramidone, antipyrine, and β-naphthoquinoline (reddish-orange color). In the presence of anabasine the precipitates obtained are a red Bordeaux color. There is a fairly good linear relation between the amount of bismuth taken and the volume of potassium iodide used in the titration.

During titration of bismuth in the presence of cinchonine and quinine, the acidity should be about 6 M with respect to sulfuric acid, while for anabasine it should be about 3 M. For titration in the presence of 8-hydroxyquinoline, pyramidone, and antipyrine the optimum acidity is 2.5 M, while in the presence of β-naphthoquinoline it is 3.5 M. 150-200 mg of the corresponding base is used in each titration.

SUMMARY

The possibility has been established and conditions have been found for the direct amperometric titration of bismuth with potassium iodide in the presence of antipyrine, with a rotating platinum microelectrode. Nitrates, sulfates, phosphates, acetates, tartrates, and citrates, as well ad EDTA-Na, do not interfere with the titration when present in amounts which are 100-200 times that of the bismuth. Chloride ions do not interfere as long as their concentration is not higher than ten times that of the bismuth. Aluminum, zinc, magnesium, cobalt, nickel chromium, manganese, and iron even in amounts which are 50-100 times that of bismuth do not interfere. Small amounts of lead (1:1), trivalent antimony (1:1), arsenic (1:1), and cadmium (3:1) do not interfere either.

The possibility has been demonstrated and conditions have been established for titrating bismuth in the presence of pyramidone or β-naphthoquinoline, and also in the presence of cinchonine, quinine, and anabasine by an anode amperometric method.

The amperometric method of determining bismuth in the presence of antipyrine has been checked on an alloy containing bismuth, cadmium, and lead.

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A STUDY OF THE INTERACTION OF QUINQUEVALENT MOLYBDENUM WITH ETHYLENEDIAMINETETRACETIC ACID

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Quinquevalent molybdenum exists in solutions with hydrochloric acid concentrations of less than 2 M in the form of yellow-brown ions [1]. At pH values higher than 3.0 the sparingly soluble hydroxide MoO_2OH is formed. During the interaction of MoO_2^+ ions with sodium ethylenediaminetetracetate (EDTA-Na, Complexon III) a yellow colored compound is formed. The stoichiometric coefficients in the equation of the reaction, as determined by the Ostromyslenskii-Job method [2], and by preparative [2], and titrimetric methods [3,4] have shown that two MoO_2^+ ions interact with one mole of ethylediaminetetracetate. The product isolated from aqueous-ethanol solutions at pH 6.0 has a composition which corresponds to the formula

$$Na_2[MoO_2(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2MoO_2]H_2O$$

Aqueous solutions of the compound are stable over a wide acidity range: from 0.5 M HCl to pH 10.0 [3]. The formation constant of the ethylenediaminetetracetate of quinquevalent molybdenum is unknown. There are no available metallo-indicators for quinquevalent molybdenum; accordingly, the latter is titrated complexometrically by titrating excess EDTA-Na with solutions of various salts, using appropriate metallo-indicators. Titration with zinc sulfate at pH 10 in the presence of eriochrome black T is a complexometric method with low selectivity [3]. The selectivity of the method can be increased by titrating with cupric sulfate, using the indicator pyridylazonaphthol at pH 4.0 [4]. It is well known that the yield of ethylenediaminetetracetates of various metals is determined by their formation constants and by the pH of the solution. If quinquevalent molybdenum could be complexed with EDTA-Na, and then excess of the latter titrated with a solution of a salt of a metal which forms a sufficiently stable compound with EDTA-Na, such a titration could be carried out in fairly acid solutions, and this in turn would ensure a method with relatively high selectivity for determining quinquevalent molybdenum.

We have determined the formation constant of the ethylenediaminetetracetate of quinquevalent molybdenum and have developed a more selective complexometric method for the determination of the latter.

Requisite Reagents. 1. Ammonium Molybdate, 1.16×10^{-2} M. 2.05 g of ammonium heptamolybdate was dissolved in one liter of distilled water. The concentration was established gravimetrically by the 8-hydroxyquinoline method [5]. 2. EDTA-Na, 2.384×10^{-2} M solution. The molarity was established against a standard solution of thorium nitrate [6]. 3. Hydrazine Sulfate – 0.5% aqueous solution. 4. Zirconyl Sulfate 1.979×10^{-2} M solution. 6.5 g of zirconyl sulfate was dissolved in one liter of 1 N sulfuric acid. The concentration of the solution was established by precipitating zirconyl hydroxide with ammonia, calcining the precipitate, and weighing it as ZrO_2. 5. Xylenol Orange – 0.05% aqueous solution.

Spectrophotometric Study of the Interaction of MoO_2^+ Ions with Ethylenediaminetetracetic Acid. Hydrazine sulfate in a solution which is 1 N with respect to sulfuric acid [3,4], on boiling for 3-5 min, ensures quantitative reduction of sexivalent molybdenum to the quinquevalent state. At room temperature the optical density of the yellow-brown colored solutions obtained remains constant for 10-15 min, and then gradually decreases. On adding EDTA-Na to the yellow-brown sulfuric acid solution of the quinquevalent molybdenum compound heated to the boil, the color changes to yellow. When stoichiometric concentrations of the reactants are used, the optical density of such solutions, after cooling to room temperature, increases with time and reaches a constant value 15 min after the solutions have been prepared.

The molar extinction coefficient of solutions of the compound of quinquevalent molybdenum with ethylenediaminetetracetic acid (ϵ_t) was determined by the saturation method. This was carried out as follows: to various volumes of 1.16×10^{-2} M ammonium molybdate solution was added 25 ml of 1 N sulfuric acid and the solutions heated to the boil; 10 ml of 0.5% hydrazine sulfate solution was then added to each solution and the solutions again boiled for 5 min. Twenty ml of 2.38×10^{-2} M EDTA-Na was added to each solution and the latter again brought to the boil.

Table 1. Molar Extinction Coefficient of Solutions of Quinquevalent Molybdenum Complexonate at 387 mμ

Initial molybdenum concentration (C_i), M	Optical density (D_i)	ϵ_t	Initial molybdenum concentration (C_i), M	Optical density (D_i)	ϵ_t
$1,16 \cdot 10^{-4}$	0,066	379	$6,96 \cdot 10^{-4}$	0,370	354
$2,32 \cdot 10^{-4}$	0,133	382	$8,12 \cdot 10^{-4}$	0,433	356
$3,48 \cdot 10^{-4}$	0,189	362	$9,28 \cdot 10^{-4}$	0,520	373
$4,64 \cdot 10^{-4}$	0,250	359	$1,04 \cdot 10^{-3}$	0,550	351
$5,80 \cdot 10^{-4}$	0,313	360	$1,16 \cdot 10^{-3}$	0,620	356

The solutions obtained were cooled to 20°, transferred to 100 ml standard flasks, diluted with water to the mark, and mixed. The optical density (D_i) of these solutions, like that of all subsequent solutions, was measured on a SF-4 quartz spectrophotometer at 387 mμ relative to distilled water. Our results confirmed published information [3] that the maximum light absorption of the compound of quinquevalent molybdenum with EDTA-Na lies in this region; quinquevalent molybdenum ions in sulfuric acid solution, as in hydrochloric acid solution [3], exhibit a relatively low absorption (see Table 2), while EDTA-Na hardly absorbs at all. ϵ_t was calculated by means of the equation where

$$\epsilon_t = \frac{D_i}{\frac{C_i}{2} l},$$

C_i is the initial molybdenum concentration, M/l; l is the path length, equal to 3 cm.

Table 2. Formation Constant of the Ethylenediaminetetracetate of Quinquevalent Molybdenum at 20°
(initial molybdenum concentration $C_i = 1.16 \times 10^{-3}$ M; initial EDTA-Na concentration 7.158×10^{-4} M. The ionic strength was varied between 0,3 and 0,7 by means of the reagents)

Initial H_2SO_4 concentration, M	Optical density of the solutions		Equilibrium concentrations of the reactants				
	Mo^V, $D_{MoO_2^+}$	Mo^V in the presence of EDTA-Na D	$[H^+]$	I	$[MoO_2^+]$	$[H_nY^{n-4}]$	$K \cdot 10^{-w}$
0,143	0,054	0,165	0,153	$4,12 \cdot 10^{-4}$	$3,36 \cdot 10^{-4}$	$4,64 \cdot 10^{-9}$	0,79
0,201	0,053	0,162	0,212	$4,04 \cdot 10^{-4}$	$3,52 \cdot 10^{-4}$	$1,56 \cdot 10^{-9}$	2,09
0,260	0,052	0,147	0,271	$3,52 \cdot 10^{-4}$	$4,56 \cdot 10^{-4}$	$7,48 \cdot 10^{-9}$	2,26
0,378	0,055	0,116	0,389	$2,26 \cdot 10^{-4}$	$7,08 \cdot 10^{-4}$	$2,57 \cdot 10^{-9}$	1,75
0,437	0,054	0,107	0,448	$1,97 \cdot 10^{-4}$	$7,66 \cdot 10^{-4}$	$1,57 \cdot 10^{-9}$	2,14
0,496	0,055	0,097	0,507	$1,56 \cdot 10^{-4}$	$8,48 \cdot 10^{-4}$	$1,05 \cdot 10^{-9}$	2,07
0,584	0,056	0,076	0,595	$7,42 \cdot 10^{-5}$	$1,01 \cdot 10^{-3}$	$6,41 \cdot 10^{-10}$	1,14

It follows from the results given in Table 1 that despite varying the amount of excess EDTA-Na from 80 to 9 times that stoichiometrically necessary, the molar extinction coefficient remains almost constant (within the limits of experimental error). Accordingly, under the conditions indicated, all the quinquevalent molybdenum is found in the form of a compound with ethylenediaminetetracetic acid. The mean value of the molar extinction coefficient $\epsilon_t = 363 \pm 8$ at a confidence level of 0,95 [7].

The complex formation constant was determined as follows. Ten ml portions of 1.16×10^{-3} M ammonium molybdate solution were introduced into a series of beakers, and the sexivalent molybdenum reduced with hydrazine sulfate as indicated above. Three ml portions of 2.386×10^{-3} M EDTA-Na solution was then added to each, the solutions were brought to the boil and then cooled to 20°. The solutions were next transferred to 100 ml standard flasks containing varying amounts of sulfuric acid, the volumes made up to the mark with water, and the solutions mixed.

In order to determine the molar extinction coefficients of quinquevalent molybdenum in sulfuric acid solutions under the same conditions, experiments were carried out with solutions containing all the components apart from EDTA-Na. Three solutions were prepared at the same time and the optical density measured 15 min after pouring the solutions together in a cell with a path length of 1 cm. The results are given in Table 2.

Sulfuric acid is a strong acid in its first dissociation stage and relatively weak in its second ($K_2 = 1.2 \times 10^{-2}$). Column 4, Table 2 contains the values of the hydrogen ion concentration obtained by adding the molar concentration of sulfuric acid and the hydrogen ion concentration calculated on the basis of the second dissociation constant.

From the results given in column 2 (constancy of optical density) it follows that on changing the sulfuric concentration from 0.143 to 0.584 M, the quinquevalent molybdenum ions are not subjected to any changes. As a result of calculation, and of a statistical treatment of the results obtained [7], it was found that the molar extinction coefficients of quinquevalent molybdenum ions at 387 mμ $\epsilon_{MoO_2^+} = 46.7 \pm 1.1$ at a confidence level of 0.95.

In accordance with published results [2-4], complex formation in the test system proceeds according to the scheme

$$2MoO_2^+ + H_{4-n}Y^{n-} = (MoO_2)_2 H_{4-n}Y^{(n-2)-}, \quad K = \frac{[(MoO_2)_2 H_{4-n}Y^{(n-2)-}]}{[MoO_2^+]^2 [H_{4-n}Y^{n-}]}. \tag{1}$$

Let us assume that the initial concentration of MoO_2^+ ions is C_1 M while that of EDTA-Na is C_2 M, and the equilibrium concentration of the complex compound is

$$[(MoO_2)_2 H_{4-n}Y^{(n-2)-}] = tM$$

Then the equilibrium concentration of $[MoO_2^+]$ will be equal to

$$[MoO_2^+] = C_1 - 2t \tag{2}$$

At 387 mμ only the complex compound and MoO_2^+ absorb, accordingly, the optical density of the solution, measured experimentally – (D), is equal to the sum of the optical densities of the MoO_2^+ ions ($D_{MoO_2^+}$) and of the complex compound (D_t)

$$D = D_{MoO_2^+} + D_t \tag{3}$$

Substituting the values of the optical densities from the expression for Beer's law in equation (3) and solving the equation obtained with respect to t, we find:

$$t = \frac{D - \varepsilon_{MoO_2^+} l C_1}{l(\varepsilon_t - 2\varepsilon_{MoO_2^+})} \tag{4}$$

Results of calculations of t by means of equation (4) and of $[MoO_2^+]$ by means of equation (2) are given in columns 5 and 6 of Table 2.

Over the hydrogen ion concentration range which we tested, ethylenediaminetetracetic acid (H_4Y) adds on an additional two hydrogen ions to its amino groups [8], and is converted into H_6Y^{2+}. Accordingly, for calculating the equilibrium concentrations of the various forms of the dissociation of ethylenediaminetetracetic acid, it is necessary to take into account the following processes and the equilibriums corresponding to them:

$$H_6Y^{2+} = 2H^+ + H_4Y \quad K_0[H_6Y^{2+}] = [H^+]^2[H_4Y], \tag{5}$$
$$H_4Y = H^+ + H_3Y^- \quad K_1[H_4Y] = [H^+][H_3Y^-] \tag{6}$$
$$H_3Y^- = H^+ + H_2Y^{2-} \quad K_2[H_3Y^-] = [H^+][H_2Y^{2-}] \tag{7}$$
$$H_2Y^{2-} = H^+ + HY^{3-} \quad K_3[H_2Y^{2-}] = [H^+][HY^{3-}] \tag{8}$$
$$HY^{3-} = H^+ + Y^{4-} \quad K_4[HY^{3-}] = [H^+][Y^{4-}], \tag{9}$$

where $K_0 = 1.24 \cdot 10^{-2}$ [8], $K_1 = 6.13 \cdot 10^{-3}$ [8], $K_2 = 1.71 \cdot 10^{-3}$ [8], $K_3 = 6.92 \cdot 10^{-7}$, $K_4 = 5.47 \cdot 10^{-11}$ [9].

In addition, taking into account all the transformations of H_6Y^{2+} one can write

$$(C_3 - f) = [H_6Y^{2+}] + [H_5Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}], \quad (10)$$

By solving equations (5-10) simultaneously with respect, e.g., to $[H_2Y^{2-}]$, $[Y^{4-}]$ respectively, we obtain:

$$[H_2Y^{2-}] = \frac{(C_3 - f) K_0 K_1 K_2 [H^+]^2}{[H^+]^6 + K_0 [H^+]^5 + K_0 K_1 [H^+]^4 + K_0 K_1 K_2 [H^+]^3 + K_0 K_1 K_2 K_3 [H^+] + K_0 K_1 K_2 K_3 K_4} \quad (11)$$

$$[Y^{4-}] = \frac{(C_3 - f) K_0 K_1 K_2 K_3 K_4}{[H^+]^6 + K_0 [H^+]^5 + K_0 K_1 [H^+]^4 + K_0 K_1 K_2 [H^+]^3 + K_0 K_1 K_2 K_3 [H^+] + K_0 K_1 K_2 K_3 K_4} \quad (12)$$

A comparison of equations (11) and (12) shows clearly $\left(\frac{[H_2Y^{2-}]}{[Y^{4-}]} = \frac{[H^+]^2}{K_3 K_4}\right)$, that the hydrogen ion concentration has a decisive effect on the yield of the different forms of ethyelendiaminetetracetic acid. Accordingly, the values of the formation constant $(MoO_2)_2H_{6-n}Y^{(n-6)}$, calculated at different hydrogen ion concentrations, will only be constant when the equilibrium concentration of the anion actually participating in the reaction leading to the formation of the compound [10] is substituted in equation (1). For all the other anions not reacting with MoO_2^{2+} ions, the values of the constants will have a systematic character which is a function of the hydrogen ion concentration. Calculations showed that only the H_2Y^{2-} anions which react with MoO_2^{2+} according to the equation enter into the reaction.

$$2\,MoO_2^{2+} + H_2Y^{2-} = (MoO_2)_2H_2Y, \; K = \frac{[(MoO_2)_2H_2Y]}{[MoO_2^{2+}]^2 [H_2Y^{-2}]} \quad (13)$$

Table 3. Yield of MoO_2H_2Y as a function of pH at $C_1 = 2 \times 10^{-3}$ and $C_2 = 1 \times 10^{-3}$ M.

pH	Yield of $(MoO_2)_2H_2Y$, %	pH	Yield of $(MoO_2)_2H_2Y$, %
0,31	10,0	4,5	98,9
1,00	87,0	5,0	98,9
2,0	97,2	8,0	95,4
		10,0	77,2

H_3Y^-, HY^{3-}, and Y^{4-} anions do not participate in the reaction. Thus the values of the formation constant of the compound $(MoO_2)_2Y^{2-}$ vary from 5.2×10^{25} to 1.1×10^{27} on changing the hydrogen ion concentration from 0.155 to 0.596 M. Results of calculations of the concentration of H_2Y^{2-} by means of equation (11) are given in column 7, Table 2. Values of the formation constant calculated by means of equation (13) are given in column 8. The constancy of the values of the constant serves as proof of the fact that the stoichiometric coefficients in the equation of the reaction, the composition of the ions from which the compound $(MoO_2)_2H_2Y$ is formed, and also the molar extinction coefficients of the MoO_2^{2+} ion and the compound $(MoO_2)_2H_2Y$ [10] have all been determined correctly. The mean value of the formation constant of $(MoO_2)_2H_2Y$ is equal to $K = (1.75 \pm 0.52) \times 10^{11}$ at a confidence level of 0.95.

We calculated the yield of $(MoO_2)_2HY_2$ (Table 3) from the values of the complex formation constant by means of equations (11) and (13).

From the results given in Table 3, and also taking into account the fact that equilibrium is established slowly in the system, it can be concluded that direct complexometric titration of quinquevalent molybdenum at 20° and with an accuracy of down to 0.1% is impossible. Nevertheless, by adding a sufficient excess of EDTA-Na, molybdenum can be quantitatively complexed as a complex compound which is suitable for spectrophotometric determination [11].

Complexometric Determination of Quinquevalent Molybdenum By Titration of Excess EDTA-Na with Standard Zirconium Sulfate Solution. In accordance with the investigations outlined above, and on the basis of published data [3,4], molybdenum can be determined complexometrically in solutions heated to 70-100°, and then only by titrating excess EDTA-Na with a suitable indicator. We decided to titrate excess EDTA-Na with zirconium sulfate solution, using xylenol orange as indicator [6].

Table 4. Results of a Statistical Treatment of Experimental Data on the Determination of Molybdenum in Solutions of its Salts and in the Presence of Impurities

Added, mg		No. of molybdenum determinations, n	Molybdenum found (mean of n determinations), mg	Mean square error	
Molybdenum	Impurity			mg	% (relative)
1,98	—	11	1,99	$\pm 6{,}4 \cdot 10^{-3}$	±3,2
9,91	—	11	9,98	$\pm 6{,}1 \cdot 10^{-3}$	±0,6
19,82	—	11	19,97	$\pm 5{,}9 \cdot 10^{-3}$	±0,29
1,93	100—UO_2^{2+}	11	1,99	$\pm 8{,}0 \cdot 10^{-3}$	±4,02
9,91	100—UO_2^{2+}	11	9.93	$\pm 5{,}9 \cdot 10^{-3}$	±0.59
11,13	10—Th^{4+}	11	11,13	$\pm 5{,}9 \cdot 10^{-3}$	±0,53
11,13	25—Al^{3+}	11	11,18	$\pm 5{,}2 \cdot 10^{-3}$	±0,46
11,13	1000—$NaNO_3$	8	11,18	$\pm 8{,}5 \cdot 10^{-3}$	±0,78

Preliminary experiments showed that the most clearly defined indicator color change from yellow to red is observed on titrating EDTA-Na solution prepared in a solution of 0.25 N sulfuric acid and 4×10^{-3}M sodium sulfate, and heated to the boil beforehand, with a solution of zirconium sulfate (1 N with respect to sulfuric acid). As a result of titrating 10 ml of 1.85×10^{-2}M EDTA-Na solution with 1.979×10^{-2} M zirconium sulfate solution under the conditions indicated above the following values for the normality of the EDTA-Na were obtained:

$1{,}880 \cdot 10^{-2}$	$1{,}876 \cdot 10^{-2}$	$1{,}880 \cdot 10^{-2}$	$1{,}874 \cdot 10^{-2}$
$1{,}882 \cdot 10^{-2}$	$1{,}880 \cdot 10^{-2}$	$1{,}880 \cdot 10^{-2}$	$1{,}884 \cdot 10^{-2}$
$1{,}880 \cdot 10^{-2}$	$1{,}884 \cdot 10^{-2}$	$1{,}880 \cdot 10^{-2}$	

The mean square error of a single determination [7] is $\pm 3 \times 10^{-5}$M or ± 0.17% (relative). Accordingly, this method was used for the determination of the concentration of EDTA-Na in pure solutions, and also, as will be shown below, in the presence of most metal ions apart from trivalent iron, bismuth, and MoO_2^{2+}, which form complex compounds with EDTA-Na in acid solutions. It was established that the titration conditions indicated can be used for determining molybdenum, by complexing it beforehand with excess EDTA-Na into the compound $(MoO_2)_2H_2Y$, and titrating excess of the EDTA-Na with zirconium sulfate. In order to check the method of determining molybdenum in solutions of its salts and in the presence of impurities, the amounts of molybdenum indicated in Table 4, in the form of an aqueous ammonium molybdate solution, were introduced into a series of 250 ml conical flasks; various amounts of the impurites were then added, followed by 25 ml of 1 N sulfuric acid. In experiments with $NaNo_3$ 4-5 g of urea was added in addition, in order to prevent oxidation of the quinquevalent molybdenum.

Table 5. Results of a Statistical Treatment of Experimental Data on the Determination of Molybdenum in Alloys with Uranium

Molybdenum content of the alloy, %	No. of determinations	Molybdenum found %	Mean square error	
			% (absolute)	% (relative)
3.60	12	3.61	$\pm 6.6 \cdot 10^{-2}$	±1.8
4.50	11	4.47	$\pm 4.2 \cdot 10^{-2}$	±0.9
8.96	8	8.96	$\pm 7.9 \cdot 10^{-2}$	±0.9

The solutions obtained were heated to the boil, and 15 ml of a 0.5% solution of hydrazine sulfate prepared in 1 N sulfuric acid added. During the boiling stage, as a result of reduction of molybdenum, the solutions acquired a brownish-yellow color. Three grams of sodium sulfate was next added to each solution, and the latter boiled for another 2-3 min. Standard EDTA-Na solution 2.384×10^{-2}M was added to the hot solutions, the amount added being sufficient to complex the quinquevalent molybdenum stoichiometrically into the compound $(MoO_2)_2H_2Y$, plus an additional 5–7 ml in excess; at this stage the color of the solution changed to a definite yellow. Hot distilled water was added immediately in such an amount as to give a final solution with a concentration of 0.25 N with respect to sul-

furic acid (the volumes of all the reagents taken for analysis being taken into account), the solution was again heated to the boil and 1 ml of xylenol orange solution added [6]. Excess EDTA-Na was titrated with the zirconium sulfate solution in sulfuric acid, with constant stirring until the yellow color changed to a distinct red which did not change for 30 sec. In the presence of Al^{3+} ions, after addition of the xylenol orange, a red color appeared, but during titration this color disappeared and did not interfere with the determination of the titration end point. Results of these determinations are given in Table 4.

The results given in Table 4 allow one to conclude that metal ions which form compounds having pk≥ 16 with EDTA-Na (Al^{3} +, Mg^{2} +, Zn^{2} +, Cd^{2} +, Mn^{2} + Co^{2} +, Pb^{2} +, La^{3} + – Nd^{3} +) should not interfere with molybdenum determination when they are present in the solution to be titrated in amounts of about one millimole.

The method has been checked on alloys of uranium with molybdenum. A 0.5-1.0 g aliquot of alloy was dissolved in 3 ml of concentrated sulfuric acid and 10 ml of nitric acid. After cessation of the turbulent reaction the solution was evaporated to the appearance of thick SO_3 fumes; it was then cooled, and diluted with water. The solution was transferred to a 100 ml standard flask and made up to the mark with distilled water. An aliquot of this solution containing 2-20 mg of molybdenum was transferred to a 250 ml conical flask and 4 g of urea added; the solution was next heated to the boil and 15 ml of hydrazine sulfate added; the solution was boiled again for a further 2-3 minutes and the procedure outlined above then followed, i.e. EDTA-Na was added and excess of it titrated with zirconium sulfate. Results of these determinations are given in Table 5.

Specially conducted experiments showed that trivalent iron, zirconium, hafnium, phosphates, flurides, oxalates, citrates, and tartrates interfere with determination of molybdenum by the given method.

The method suggested permits determination of the molybdenum content of the solution obtained after decomposition of test material to be carried out in 20 min.

SUMMARY

The molar extinction coefficient of solutions of the compound of quinquevalent molybdenum with ethylenediaminetetracetic acid ($MoO_2)_2H_2Y$ is 363 ± 8 at 387 mμ, while the complex formation constant is $1.75 \pm 0.52 \times 10^{11}$ at a confidence level of 0.95.

A variant which has been developed for the complexometric determination of quinquevalent molybdenum is based on complexing the molybdenum with EDTA-Na, and titrating excess of the latter with zirconium sulfate solution, using xylenol orange as indicator.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF URANIUM

COMMUNICATION 3. PHOTOMETRIC DETERMINATION OF URANIUM IN ORES AND THEIR PROCESSED PRODUCTS BY MEANS OF ARSENAZO I*

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Arsenazo I (benzene-2-arsonic acid-<1-azo-2>-1,8-dihydroxy-naphthalene-3,6-disulfonic acid) forms with the uranyl ion at pH 4-8 a blue colored complex which is readily destroyed by hydrogen peroxide [1]. Many elements react with arsenazo under these conditions, and accordingly, in order to determine uranium in ores, it must be isolated in a pure state, free from impurities [2].

Table 1. Determination of Uranium in ores after Its Separation by Partition Chromatography

Uranium content, %		Found by the sug. method
No. of determinations	Specified value	
0,083±0,001	0,083±0,001	10
0,237±0,006	0,240±0,001	10
0,560±0,011	0,570±0,002	10
0,059±0,004	0,061±0,001	10
0,070±0,001	0,069±0,001	10

Table 2. Determination of Uranium in Processed Products from Uranium Ores

Uranium content %		Uranium content %	
By the suggested method	By other meth.	By the suggested method	By other meth.
0,019	0,019	0,012	0,013
0,013	0,014	0,013	0,012
0,013	0,015	0,013	0,015
0,012	0,012	0,012	0,010

In the present article a description is given of a photometric determination of uranium with arsenazo I, after a preliminary separation of uranium from the impurities by a partition chromatographic method and by ion exchange on SG-1 carboxyl resin.

Burstall and Wells [3] were the first to describe a partition chromatographic method for purifying uranium [3]. We used a variant of this method suggested by Markov [4]. In this variant the carrier is chemically pure silica gel, while the stationary phase is a saturated solution of ammonium nitrate acidified with nitric acid to an acidity of 0.5 N with respect to nitric acid, and the mobile phase is ethyl ether also acidified with nitric acid to a value of 0.5 N.

Using a 6-7 cm column of the purifying layer (silica gel soaked with the stationary phase) and an ether throughput of 1-2 ml/min, only 40-45 ml of ether is required for separating the uranium completely from impurities, in contrast to the 150-200 ml recommended in Burstall and Wells' method. In the absence of interfering anions (F^-, Cl^-, SO_4^{2-}, and other ions which complex uranium into a complex which is insoluble in ether) only vanadium, in the form of its red colored peroxide compound, moves with the uranium at an appreciable velocity along the column. The rate at which vanadium moves along the column is, however, low compared with that of uranium, and does not interfere with determination of the latter. At high vanadium contents of samples Markov recommends its reduction with hydrazine nitrate. Chemically pure silica gel** with a particle size of 0.5 mm was calcined at 450° for one hour before use. A saturated solution of ammonium nitrate which was 0.5 N with respect to nitric acid (solution I) was prepared by adding 50 ml of concentrated nitric acid per liter of a saturated aminonium nitrate solution. The solution obtained was titrated with alkali and its acidity adjusted to 0.5 N either by addition of acid or a saturated solution of ammonium nitrate. To prepare a similar solution (solution II), with an acidity of 1.15 N with respect to nitric acid, 115 ml of concentrated nitric acid was added per liter of saturated ammonium nitrate solution. Diethyl ether, 0.5 N with respect to nitric acid, was prepared by shaking equal volumes of ether and solution II in a separating funnel for 2-3 min.

*For communication 2, see Zh. analit. khimii 16, 60 (1961).

** The silica gel was prepared according to Markov and Volkova's method [4].

Uranium was determined in ores as follows. An aliquot of sample containing 50-100 μg of uranium was decomposed with nitric acid.

When other methods are used for decomposing test material, anions which interfere with extraction of uranium must be removed.

Anions of volatile acids were removed by evaporating the sample four to five times with nitric acid; it was freed from other anions by precipitating the hydroxides and subsequently dissolving these in nitric acid.

After the sample had been decomposed and the insoluble residue had been removed, the solution was evaporated to the damp salt state. 0.5 ml of solution I was added, followed by 1-2 ml of silica gel, which, after mixing with the solution should retain its friable character. Otherwise, a little more of it should be added.

Uranium was separated from impurities in the chromatographic column. Two ml of solution I and 6-7 ml of silica gel were first introduced into the column. Next the reducing layer of 1-1.5 ml of silica gel saturated with 5% hydrazine nitrate was inserted, followed by the partitioning layer—silica gel saturated with the test solution. Ether was passed through a column prepared in this way at the rate of 1-2 ml/min. The ethereal solution of uranyl nitrate issuing from the column was collected in a beaker containing 10-15 ml of water. Completeness of elution of uranium was controlled by a luminescence method. The ether was removed by careful evaporation on a water bath and the uranium in solution determined photometrically with arsenazo I [5]. For this purpose the solution was transferred to a 50 ml standard flask, in which it was neutralized with ammonia, using methyl red as indicator; two drops of HCl (1:1), 1 ml of 25% urotropine solution, and 2 ml of 0.1% arsenazo I solution were added, and the volume made up to the mark with water. After 10-15 min the optical density of the solution was measured on a FÉK-M photocolorimeter fitted with red filter and using a 2 cm cell.

The reference solution used was one containing all the reagents apart from uranium. Ten drops of 30% H_2O_2 was added to the cells containing the test and reference solutions, the solutions were stirred and the optical density measured again. The uranium content was determined from a calibration curve constructed in a similar way using solutions with 20, 40, 60, 80, and 100 μg uranium in 50 ml of solution.

Results for the determination of uranium in a series of ore standards and processed products from uranium ores are shown in Table 1 and 2.

The comparatively high sensitivity of the method permits it to be used for determining small amounts of uranium (0.001-0.1%) with sufficient accuracy in ores, in those cases where other methods do not give reliable results. Nevertheless, because of the necessity of using ether, and the need for specially prepared silica gel, the method has limited possibilities for its wide application in plant laboratories and for control purposes.

We have tried to overcome the disadvantages of the method described above for purifying uranium by using ion exchange on the carboxyl ion exchange resin SG-1 for this purpose.

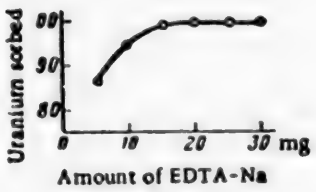
Comparatively little work has been devoted to the study of the behavior of uranium on cation exchange resins, and its use for analytical purposes. Ishimori and Okuno [6] have described the behavior of uranium on the strongly acid cation exchange resin Dowex 50. Kennedy and Davies [7] used a phosphoric resin for separating uranium from heavy metal; Fodor [8] used the cation exchange resin Amberlite URC-50 for separating uranium from impurities, using sodium ethylenediaminetetracetate (EDTA-Na). A similar method has been described by Ryabchikov, Palei, and Mikhailova [9] in which the cation exchange resin KU-2 was used. The principle of the method consists in complexing elements which interfere with the quantitative determination of uranium by means of EDTA-Na, followed by selective sorption of the uranium with a cation exchange resin. Our work consisted in establishing the conditions for selective sorption of uranium by the carboxyl resin SG-1 from solutions containing EDTA-Na.

7-8 ml of resin SG-1 (particle size 0.4-0.6 mm) in the swollen state was introduced into a chromatographic column with a diameter of 10 mm and was treated with 10% HCl until the eluate gave a negative reaction for Fe^{III}, and was finally washed with distilled water until the eluate gave a negative reaction for Cl^-. A column prepared in this way was kept under distilled water.

A standard solution of uranyl nitrate with a concentration of 1 mg/ml and a 5% aqueous solution of EDTA-Na were used in our work. 10% HCl was used for eluting the uranium from the column.

The method of investigation consisted of the following. A solution of a definite pH value containing uranium, a foreign element, and the requisite amount of EDTA-Na was passed through the resin column at a rate of about

1 ml/min. The column was then washed with 100-150 ml of distilled water and the uranium eluted from the column by passing 50-75 ml of HCl, and then distilled water until the total volume of eluate was 100 ml (the eluate was collected in a 100 ml standard flask). The uranium content of the eluate was determined as described above.



The relation between sorption of uranium from solutions containing PO_4^{3-}, and the amount of EDTA-Na. 5 mg of uranium and 10 mg of phosphorus (molar ratio 1:17) were taken for each determination.

Experiments on the sorption of uranium from solutions with varying pH values, in the presence of EDTA-Na, showed that sorption of 10 mg of uranium is quantitative only at pH≥ 3.

The pH limit at which the column operates can be lowered to 1.5 when the uranium is sorbed on the resin in the NH_4-form. The resin was converted to its NH_4- form by washing it with 200 ml of 0.1-0.5% ammonium nitrate. This same solution can be conveniently used for washing the column after sorption. The resin does not swell under these conditions, as occurs when the column is washed with water.

The effect of a series of ions: PO_4^{3-}, SO_4^{2-}, MoO_4^{2-}, VO_3^-, F^-, Fe^{III}, Al, Ti, Ca on the sorption of uranium was studied.

MoO_4^{2-} and WO_4^{2-} do not interfere with uranium sorption. When vanadium is present, sorption of 10 mg uranium is quantitative only when the pH is 3.5-4.5 and in the presence of a sufficient excess of EDTA-Na (not less than 100 mg per 1 mg uranium). The effect of other elements was only studied over the pH range 3.5-4.5.

Completeness of uranium sorption from solutions containing PO_4^{3-} ions also depends on the EDTA-Na concentration of the solution (see diagram).

Table 3. Determination of Uranium in Ores after Its Sorption on SG-1 Cation Exchange Resin

Uranium content, %		By the specified method	Uranium content, %		By the specified method
No. of determinations	Specified content		No. of determinations	Specified content	
0,070±0,001	0,069±0,001	18	0,083±0,001	0,081±0,005	8
0,103±0,002	0,102±0,001	15	0,059±0,004	0,059±0,001	15
0,560±0,011	0,557±0,004	11	0,220±0,01	0,214±0,002	5

Since we did not have to deal with samples containing much phosphorus, its effect at molar ratios to uranium greater than 17:1 was not examined.

SO_4^{2-} ions start to interfere at a molar ratio of UO_2^{2+}: SO_4^{2-} = 1:200, while F^- starts to interfere at a molar ratio of 1:10, even when an appreciable excess of EDTA-Na is present. Interference from elements of the second group on the sorption of uranium and on its subsequent determination with arsenazo I was not observed.

Uranium was determined in ores as follows. A 0.5 g aliquot of sample (for uranium contents of 0.01-0.1%) was decomposed with hydrochloric acid and hydrogen peroxide. After removal of the insoluble residue, 15-20 ml of 5% EDTA-Na solution was added and the solution alkalinified with ammonia until the color of the solution changed (pH 7). When the solution was turbid at this stage it was acidified again, and some additional ml of EDTA-Na solution added; it was finally alkalinified to a pH of 3.5-4.5 using an external universal indicator; this solution was passed throuhg a column of SG-1 resin in the NH_4-form at the rate of 1 ml/min. The column was next washed with 200 ml of 0.1-0.5% ammoniumnitrate solution at the rate of 2-3 ml/min and the uranium eluted with 75 ml of HCl (10% by volume), the eluate being collected in a 100 ml standard flask. The volume of the solution was made up to the mark with distilled water which had been passed through the same column, and the uranium content determined by means of arsenazo I.

The column was restored to its working state by passing ammonium nitrate solution through it until the pH of the solution issuing from the column was 3.5-4.5. The method is simple to carry out and allows 10-15 samples to be dealt with simultaneously. Table 3 contains results for the determination of uranium in a series of ore standards.

SUMMARY

A photometric method has been developed for the determination of uranium in ores, and in processed products from these ores by means of arsenzao I. Uranium is removed beforehand from impurities either by a partition chromatographic method, or by ion exchange on the cation exchange resin SG-1 in the presence of EDTA-Na.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COBALT AS COBALT (III) DIETHYLDITHIOCARBAMATE

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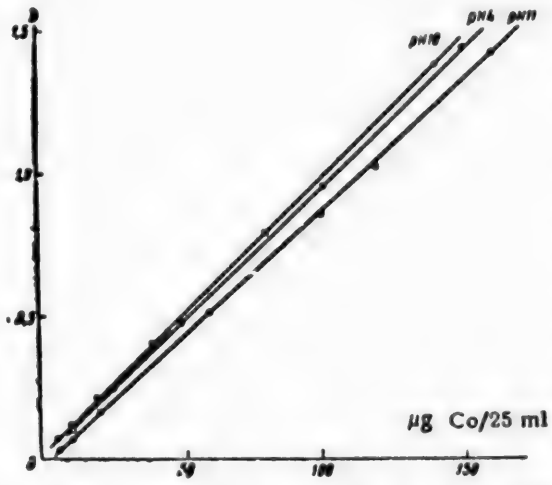
There are numerous and diverse methods in existence for the photometric determination of small amounts of cobalt. The ones most widely used are those based on formation of innercomplex (and salt form) compounds with organic reagents. Most of them, however, do not solve the problem of determining cobalt in the presence of nickel, which has similar chemical properties. Introduction of additional operations for removing nickel complicate the methods appreciably and render them unsuitable.

We have tried to develop a rapid, accurate, and sensitive method for the determination of small amounts of cobalt in the presence of large amounts of nickel, copper, manganese, zinc, and other elements. The method is based on the results of a study of the chemical interaction of sodium diethyldithiocarbamate with the ions of various metals and the behavior of the interaction products toward organic solvents, in particular, to carbon tetrachloride.



It is known [1-5] that the solubility of metal diethyldithiocarbamates in organic solvents is strongly dependent on the pH of the aqueous solution. By selecting the pH of the solution and using various masking agents it is possible to extract various diethyldithiocarbamates selectively. Bode [3, 4] as a result of a systematic study of the extractability of diethyldithiocarbamates by various organic solvents in the presence of masking agents, and in their absence, established that the diethyldithiocarbamates of Ag, Bi, Co, Cd, Cu, Hg, Ni, Pb, Pd and Tl are extracted at pH's greater than 11, while of these elements Ag, Bi, Hg, Pd, and Tl do not interact with sodium ethylenediaminetetracetate (EDTA-Na). Ni and Mn form the most stable complexes with EDTA-Na, so that they cannot be extracted from solution in the presence of this masking agent, whatever the pH, while Co, Fe, and Zn are extracted at pH< 6.

On shaking a solution of Co^{II} with diethyldithiocarbamate and CCl_4 in air, the Co^{III} diethyldithiocarbamate which is always formed is quantitatively extracted from solution at pH 4-11. The solution of Co^{III} diethyldithiocarbamate in CCl_4 has two absorption maxima at 323 and 367 mμ, which can be used for the quantitative determination of cobalt.

The selectivity of diethyldithiocarbamate methods can be enhanced by replacing one of the carbamates by others as a function of their stability. Thus divalent mercury almost quantitatively replaces many elements (with the exception of nickel) from their diethyldithiocarbamates, while cobalt is not replaced[6].

In order to establish the possibility of determining cobalt photometrically as its diethyldithiocarbamate in CCl_4* a preliminary series of experiments was carried out which showed that Co^{III} diethyldithiocarbamate passes

*All measurements were made on a FÉK-N-54 photocolorimeter fitted with filters, λ_{max} = 365 mμ, in 1 cm cells.

almost completely into the organic phase after shaking for two minutes with CCl_4, and that its solution is stable for 3 hr. During extraction in a separating funnel 20 ml of buffer mixture with pH 10.17•, 0.5 ml of cobalt salt solution (50 μg), and 1 ml of 0.5% sodium diethyldithiocarbamate were mixed and shaken with 20 Ml CCl_4. Since extraction of metal diethyldithiocarbamates is strongly dependent on pH, experiments were carried out to establish the optimum pH range for extraction of cobalt diethyldithiocarbamate. For this purpose the optical density of extracts with varying pH (4, 10, 11)•• and increasing cobalt contents were determined. As the diagram shows, maximum extraction is observed at pH 4-10; over this range the extent of extraction is almost the same. The fact that the curve is linear indicates that solutions of Co^{III} diethyldithiocarbamate in CCl_4 conform to Beer's law throughout the whole cobalt concentration range studied (0 - 150 μg in 25 ml). The sensitivity is 0.2 μg cobalt in one ml.

Table 1

Ion	Me + DDTC - Na		Me + DDTC-Na + EDTA-Na		Ion	Me + DDTC - Na		Me + DDTC-Na + EDTA-Na	
	pH 4	pH 10	pH 4	pH 10		pH 4	pH 10	pH 4	pH 10
Co^{II}	+	+	+	—	Cr^{III}	Wkly.	—	—	—
Ni^{II}	+	+	Weakly	—	Al^{III}	—	—	—	—
Mn^{II}	+	+	"	—	As^{V}	—	—	—	—
Fe^{II}	+	+	+	—	Ca^{II}	—	—	—	—
Zn^{II}	+	+	+	—	Mg^{II}	—	—	—	—
Hg^{II}	+	+	+	+	Ti^{IV}	—	—	—	—
Cu^{II}	+	+	+	+	V^{V}	+	—	—	—
Bi^{III}	+	+	+	+					

Table 2

Co intro. μg/25 ml	Hg^{II} intro., ml	Co found μg/25 ml	Error
50	0,5	51,0	+1,0
50	1,0	49,5	—0,5
50	1,5	52,7	+2,7
50	2,0	49,0	—1,0

Table 3

Element	Max. amt. of element replaced by 2 ml of 0.5% Hg^{II} sol., μg	Shaking time, min
Ni	400	4
Ni	600	2
Mn	400	4
Mn	600	2

To confirm our conclusion on the completeness of extraction of cobalt over the pH range 4 to 10, we used the radioactive isotope of cobalt Co^{60} with a half-life period of 5.24 years. The radioactivity of the Co^{60} solution was measured on a type B apparatus with a γ-counter. Proper functioning of the apparatus for the use was checked on a standard uranium sample. Measurements were made in a quartz cell which was fitted directly into the counting tube. The counter and cell were protected with a lead "chamber" with 44 mm thick walls. Extraction was carried out as described above. These experiments showed that the extent to which cobalt is extracted at pH 10 is 99.66%, while at pH 11 it is only 76.8%. A similar result was obtained at pH 4.

In order to establish to what extent the diethyldithiocarbamates of accompanying elements is extracted with CCl_4, and to establish the conditions for eliminating interference from these elements on cobalt determination, we carried out two series of experiments at pH 4 and 10. One series of experiments was carried out to study the interaction of various metal ions with sodium diethyldithiocarbamate, and the other with sodium diethyldithiocarbamate in the presence of EDTA-Na. The results obtained are given in Table 1.

In addition, we checked on the substitution (replacement) series. Twenty ml of buffer solution with pH 4 was introduced into a separating funnel; this was followed by 0.5 ml of a solution of a cobalt salt (or known amounts of the solutions of the salts of other elements), and 2 ml of 0.5% sodium diethyldithiocarbamate, and the cobalt diethyldithiocarbamate (or the carbamates of the other elements) formed extracted with 10 ml CCl_4 for 2 min. A solution of mercuric acetate (0.5%) was then added and the mixture shaken again for 2 or 4 min. The results obtained are given in Tables 2 and 3.

•A mixture of equal volumes of 0.1 M sodium carbonate and 0.1 M hydrochloric acid.

•• The solutions were treated in the same way as that described above, except that the reference solution (CCl_4) was treated in the same way as the cobalt salt solution.

Table 4

Introduced, μg/25 ml					Co found μg	Error μg	Introduced, μg/25 ml					Co found μg	Error μg
Fe	Cu	Mn	Ni	Co			Fe	Cu	Mn	Ni	Co		
			4000	5	6	+1		800		4000	100	98	−2
			4000	25	27	+2		1000		4000	100	93	−7
			4000	50	52,5	+2,5	600			4000	50	50,5	+0,5
			4000	100	97	−3	800			4000	50	58,5	+8,5
		4000		50	46,8	−3,2	600	800		4000	50	50,5	+0,5
		4000		100	99	−1	600	800	4000		50	46,5	−3,5
		4000		140	138,5	−1,5	600	800	2000	2000	50	50,5	+0,5
		2000	2000	60	62	+2							

Table 5

Taken, μg/25 ml					Co found, μg	Error μg	Taken, μg/25 ml					Co found μg	Error μg
Mn	Cu	Ni	Fe	Co			Mn	Cu	Ni	Fe	Co		
			4000	5	3	−2		400		4000	50	55	+5
			4000	50	52,5	+2,5		200		4000	50	52,5	+2,5
			4000	140	139,5	−0,5	400			4000	50	55,5	+5,5
		400	4000	50	56	+6	200			4000	50	48	−2
		200	4000	50	52	+2	200	200	200	4000	50	52	+2

Table 6

Taken, μg/25 ml					Co found μg	Error μg	Taken, μg/25 ml					Co found μg	Error μg
Mn	Fe	Ni	Cu	Co			Mn	Fe	Ni	Cu	Co		
			3000	50	50,5	+ 0,5			200	3000	50	53	+ 3
			3000	130	132	+ 2	200		200	3000	50	52,5	+ 2,2
			4000	50	38,5	−11,5	200	200	200	3000	0	0	0

Table 7

pH	Taken μg/25 ml		Optical density, D	pH	Taken μg/25 ml		Optical density, D
	Co	Zn			Co	Zn	
10	50	0	0,48	4	50	5000	0,29
10	50	5000	0,08	4	50	4000	0,40
4	50	0	0,48	4	0	4000	−0,09

As the results in Table 1 show, on adding sodium diethyldithiocarbamate and EDTA-Na to the test solution, and changing the pH from 10 to 4, small amounts of cobalt can be determined in the presence of many elements. The effect of nickel and manganese, which, despite altering the pH of the medium and adding EDTA-Na, are partially extracted as their carbamates with cobalt, can be eliminated, as is evident from the results given in Tables 2 and 3, by replacing them from their carbamates by mercuric salts. By using such a technique, not one of the elements which we studied hardly affects determination of cobalt.

Determination of Cobalt in the Presence of Large Amounts of Ni and Mn is based on the fact that Co, Mn, and Ni are masked by EDTA-Na at pH 10, and thereby can be completely separated from copper, bismuth, and other elements. Subsequently, by altering the pH of the medium from 10 to 4, cobalt diethyldithiocarbamate is extracted. During this stage iron and some nickel and manganese are also extracted. Their influence can, however, be eliminated by replacing them with Hg^{2+} ions, with formation of colorless Hg^{II} diethyldithiocarbamate, while Co^{III} is not extracted under the same conditions.

Table 8

Intro. μg/25 ml		Co found μg	Error μg
Zinc	Cobalt		
5000	0	0	0
5000	5	5,5	+0,5
5000	25	24,0	−1,0
5000	100	101,0	+1,0
5000	140	136,5	−3,5

Table 9

Sample No.	Specified Co content, %	Co found, %	Mean value, %
1	0.78	0.75; 0.78	0.77
2	0.025	0.023; 0.021; 0.024	0.023
3	0.015	0.018; 0.014; 0.014	0.015
4	0.014	0.013; 0.012; 0.012	0.012

When EDTA-Na is present in solution together with sodium diethyldithiocarbamate, simultaneous formation of cobalt carbamate and complexonate is possible, since they possess almost equal stability. The stability of the carbamate is somewhat higher, so that at pH< 6 cobalt complexonate can change into its carbamate in the presence of a sufficient excess of sodium diethyldithiocarbamate. Accordingly, on isolating cobalt with sodium diethyldithiocarbamate in the presence of EDTA-Na, a considerable excess of the latter is necessary. It was established that 4 ml of a 1% solution of sodium diethyldithiocarbamate is necessary for masking 4 mg nickel and 150 μg cobalt.

On the basis of the results of the experiments described above cobalt was determined as follows. Four ml of a 1% solution of EDTA-Na and solutions containing known amounts of cobalt and other elements were introduced into a separating funnel. After shaking for two minutes 16 ml of buffer solution (pH 10), 4 ml of 0.5% sodium diethyldithiocarbamate solution, and 1 ml of glacial acetic acid were added, and extraction carried out for 2 min with 10 ml CCl_4. Two ml of a 0.5% solution of mercuric acetate solution was then added and the funnel shaken a further 4 min. The extract was transferred through a dry filter into a 25 ml standard flask. The extraction was repeated, the second extract combined with the first, and the volume made up to the mark with CCl_4. After mixing, the optical density was measured in a cell with a path length of 1 cm at 365 mμ, relative to the extract obtained from a solution not containing cobalt which had been and treated in the same way as the test solution. When copper and metals similar to it were present, after addition of the buffer solution, 2 ml of 0.5% sodium diethyldithiocarbamate solution was added. The precipitate of the carbamates of copper and the other elements were removed by extraction with CCl_4. Determination of cobalt was then carried out as described above.

From the results obtained (Table 4) it is clear that iron, copper, nickel, and manganese do not interfere with the determination at ratios of Co:Ni:Mn = 1:800:800; Co:Cu = 1:160, and Co:Fe = 1:120. Microamounts of Ag, Bi, Cd, and Pb do not interfere (according to the results in Table 1).

Determination of Cobalt in the Presence of Large Amounts of Iron. As previous experiments have shown, during determination of cobalt with sodium diethyldithiocarbamate, iron is replaced by mercuric ions only at ratios of Co:Fe = 1:120.

Pyatnitskii [7] has shown that at pH 10 iron is masked by tartaric or citric acid. Under these conditions cobalt is not affected. A check which we carried out showed that the pH of the medium must be strictly controlled. This limits the possibility of using this method of masking iron. Pribil et al [8] used thoron (pyrocatecholdisulfonic acid) as a masking agent. We used pyrocatechol, which readily masks iron in weakly ammoniacal media, for this purpose. Determination was carried out as follows. Four ml of 1% pyrocatechol solution and the test solution containing known amounts of cobalt and interfering elements were introduced into a separating funnel. Ammonia was then added dropwise until the solution had a red color, 15 ml of buffer solution (pH 10) and 4 ml of 0.5% sodium diethyldithiocarbamate were then added. The solution was next extracted with 10 ml of CCl_4 for 2 min. The extract was transferred to another funnel containing 15 ml of buffer solution (pH 10) and 2 ml of 0.5% mercuric acetate solution, and the funnel shaken for 2 min. The extract which had been freed from impurities was filtered through a dry filter into a 25 ml standard flask. The extraction was repeated. The combined extracts were made up to the mark with CCl_4, and the optical density measured in a 1 cm cell at 365 mμ, relative to CCl_4 treated in the same way. Results of these determinations are given in Table 5.

By using pyrocatechol it is possible therefore to determine cobalt in the presence of iron, manganese, copper, and nickel.

Determination of Cobalt in the Presence of Large Amounts of Copper. Copper, in contrast to cobalt, does not interact with EDTA-Na, and can be precipitated with sodium diethyldithiocarbamate at pH 10 and removed by sub-

sequent extraction with CCl_4; under these conditions cobalt remains in the aqueous solution in which it is determined. In those cases where the solution also contains, in addition to copper, elements which, like cobalt, form complexonates, these elements are replaced from their carbamates by means of a mercuric salt. The determination was carried out as follows. Two ml of a 1% solution of EDTA-Na, solutions containing known amounts of cobalt and other elements, 17 ml of buffer solution, and 2 ml of a 2% solution of sodium diethyldithiocarbamate were mixed in a separating funnel. Copper carbamate was then extracted with CCl_4. Extraction was repeated until the extract obtained was colorless. A further 2 ml of 2% sodium diethyldithiocarbamate solution was then added, and the pH adjusted from 10 to 4 by adding 1 ml of glacial acetic acid. The colored precipitate was extracted with 10 ml of CCl_4. Two ml of 0.5% mercuric acetate solution was added and the funnel shaken for 2 min. The purified extract was transferred through a dry filter into a 25 ml standard flask. The extraction was repeated. The volume was made up to the mark with CCl_4 and the optical density measured relative to an extract obtained from a blank run. The results obtained are given in Table 6. It follows from these that cobalt can be determined in the presence of 600 times its amounts of copper and 40 times its amount of nickel, iron, and manganese.

Determination of Cobalt in the Presence of Large Amounts of Zinc. Zinc, like cobalt, in the presence of EDTA-Na is precipitated by sodium diethyldithiocarbamate at pH< 6, and is extracted together with cobalt. Nevertheless, since zinc carbamate does not exhibit appreciable absorption in the ultraviolet, cobalt can be determined in the presence of zinc without a preliminary separation of these elements. Our experiments have shown, however, that in the presence of zinc, the optical density of the solution decreases (Table 7), presumably because of the interaction of zinc with the free sodium diethyldithiocarbamate in solution, as a result of which the optical density of the reference solution increases relatively (since sodium diethyldithiocarbamate exhibits appreciable absorption at 365 mμ, the results for cobalt are low). Accordingly, zinc must either be removed before determination, or must be replaced by addition of a mercuric salt solution; for this purpose extraction must be carried out at pH 4, since at pH 10 the basic zinc salt formed as the result of hydrolysis adsorbs the cobalt.

On the basis of experiments which we carried out, the following analytical procedure can be suggested. Nineteen ml of buffer solution (pH 4) and a solution containing cobalt and zinc are introduced into a separating funnel. Four ml of a 2% solution of sodium diethyldithiocarbamate is then added and the mixture extracted with about 10 ml of CCl_4; having added 2 ml of 0.5% mecuric acetate solution, the funnel is shaken up again for a further 2 min. The extract is next transferred through a dry filter into a 25 ml standard flask. Extraction is repeated. The extracts are combined and their volume made up to the mark with CCl_4; the optical density is then measured relative to CCl_4 treated in the same way. Results of cobalt determination are given in Table 8.

In order to check on the method, we analyzed samples of nickel metal (sample No. 1), copper-zinc sulfide ores (samples Nos. 2 and 3), and an ore with a high content of rare earths (42.2%; sample No. 4).

Determination of Cobalt in Nickel Metal. An aliquot was dissolved on heating in a mixture of acids [10 ml HCl (1:1) + 5 ml HNO_3]. After evaporating to dryness the residue was dissolved in hot water, the solution transferred to a 100 ml standard flask, and its volume made up to the mark with water. A 2 ml aliquot of this solution was pipetted into a separating funnel and cobalt determined by the procedure outlined (determination of cobalt in the presence of nickel and manganese). The results are given in Table 9.

Determination of Cobalt in Rocks. An aliquot of 0.5-1.0 g was decomposed with a mixture of hydrochloric and nitric acids on heating. The solution was diluted with an approximately equal volume of water; it was then cooled, and after silica was filtered off was evaporated to dryness. The dry residue was moistened with a small amount of hydrochloric acid, and again evaporated to dryness to remove the nitric acid completely. The residue was dissolved in 8-10 ml of 6 N hydrochloric acid and the iron removed by extraction with 10 ml of ether saturated with 6 N HCl. The ethereal layer was discarded. The aqueous layer was evaporated to the moist salt stage, the salts were dissolved in hot water and the solution obtained filtered into a 50 ml standard flask. An aliquot (5-10 ml) was transferred to a separating funnel, and 4 ml of EDTA-Na and 11 ml of buffer solution (pH 10) added; ammonia was finally added dropwise until the pH was 10 (indicator paper). Analysis was subsequently carried out according to the procedure outlined for the determination of cobalt in the presence of nickel, manganese, and copper (samples 2 and 3), or by the procedure given for the determination of cobalt in the presence of copper (sample No. 4): Since sample No. 4 contained 42.2% of rare earths in addition to iron, copper, zinc, and calcium, the rare earths were removed as their oxalates [9] before removing the iron. As the results given in Table 9 show, the suggested method gives completely satisfactory results.

SUMMARY

A study has been made of the conditions necessary for the photometric determination of small amounts of cobalt in the form of Co (III) diethyldithiocarbamate at λ_{max} = 365 mμ. The optimum pH range for extracting cobalt carbamate with carbon tetrachloride has been established by means of Co^{60} (pH 4.0 - 10.0).

A photometric method has been developed for the determination of small amounts of cobalt in the presence of large amounts of nickel, manganese, copper, iron, and zinc, in which the cobalt is determined in the form of a solution of cobalt (III) diethyldithiocarbamate in CCl_4. The sensitivity of the method at λ_{max} = 365 mμ is 0.2 μg Co/ml. Solutions conform to Beer's law over the range 0 - 150 μg/25 ml. Satisfactory results have been obtained during the determination of cobalt in samples of nickel metal and rocks.

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DETERMINATION OF FREE NITRIC ACID IN URANYL NITRATE TRIBUTYLPHOSPHATE SOLUTIONS

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The absence of analytical methods of determining free nitric acid in organic solvents (a mixture of tributyl phosphate with CCl_4 or saturated high boiling hydrocarbons-SHBH *) compels the research worker to transfer the contents of the organic phase into an aqueous solution, in which the free nitric acid is determined by potentiometric or conductometric titration. Such a method, however, is not justified, because of the long time taken to carry it out, but mainly because of the appreciable errors which arise during determination of acidity, since in the final result this reduces to the old problem of determining acidity in the presence of one or several hydrolyzable salts [1-7].

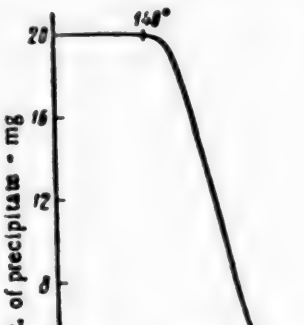

Fig. 1. Thermogravigram of acridine nitrate.

The use of complexing agents [2,3] and heavy metal salt precipitants [6,7] appreciably lengthens the course of an analysis and does not lead to the desired effect in the case of low concentrations of free acid. Indirect methods of determining acidity (the use of cation exchange resins in the H-form, H_2O_2, etc) are also not free from the disadvantages listed above.

We have tried to use the simplest aliphatic and cyclic amines for the detection and quantitative determination of nitric acid directly in tributylphosphate solutions.

During the isolation of amines from aqueous or mixed (water and organic solvent) solutions in organic syntheses, wide use is made of neutralization reactions leading to the formation of sparingly soluble salts of an organic base and a mineral acid. Hydrochloric acid is most frequently used for this purpose, but, generally speaking, the choice of acid depends to a considerable extent on the type of amine, and on the medium in which it is found. It is obvious, that if, on the other hand, the mineral acid is in the organic phase, then its presence can be detected by means of amines. Information has been published [8] to the effect that salts of aliphatic amines of high molecular weight (of the order of 250-600) are considerably more soluble in organic solvents of low polarity, and are used during the extraction separation of heavy metals [8,9]. Accordingly, we have only examined the simplest and most readily available representatives of the class of aliphatic and cyclic amines.

Although tributylphosphate solutions of uranyl nitrate always contain some water in the form $TBP \cdot H_2O$ [10] it might be expected that the addition of a very weak organic base to such solutions should not lead to chemical processes related to the hydrolysis of uranyl nitrate.

Qualitative tests (Table 1) showed that many of the amines tested form precipitates with the nitric acid present in tributylphosphate solutions. The simplest representatives of the aromatic amines proved to be good precipitants. Of these, the one of greatest practical interest was acridine (2,3-dibenzopyridine), the sensitivity of which to HNO_3 proved to be highest (the usual weighting effect of an organic molecule in a homologous series), while its salt form – acridine nitrate – is very stable under ordinary conditions. Thermogravimetric study showed that this compound (Fig. 1) can be heated up to 120° without suffering appreciable decomposition or volatilization; in addition, it was established that it does not possess any appreciable hygroscopicity.

The composition of the precipitate was determined by conductometric and indicator titration, and also gravimetrically.

*SHBH – saturated high boiling hydrocarbons.

Table 1

Amine* (about 0.01 M solution in CCl_4)	20% tributylphosphate in CCl_4 containing 0.05 M HNO_3	20% tributylphosphate in SHBH containing 0.05 M HNO_3
Ethylamine	–	White precipitate
Diethylamine	White precipitate	" "
Allylamine	No precipitate formed	–
Aniline	White precipitate	White precipitate
p-Anisidine	" "	" "
α, β-Naphthylamines	" "	" "
Pyridine	" "	" "
Quinoline	" "	" "
Quinaldine	" "	" "
Acridine	Yellow precipitate	Yellow precipitate
Diphenylamine	No precipitate formed	No precipitate formed
Benzidine	White precipitate	White precipitate
Nitron	No precipitate formed	No precipitate formed

*5-7 ml of a carbon tetrachloride solution of the amine was added to about 1 ml of tributylphosphate solution containing HNO_3 in each case.

In the first instance an accurately weighed aliquot of acridine nitrate, obtained by precipitation in tributylphosphate solutions, was taken, and the amount of nitric acid present calculated on the basis of the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$. The aliquot was then dissolved in a mixture of $H_2O - CH_3OH$ (4:1) and titrated with an aqueous alkali solution. The equivalence point was clearly defined both when visual titration with and without an indicator (phenolphthalein) was used.

In the second instance, knowing the exact concentration of nitric acid in a 4% solution of tributylphosphate (CCl_4 and SHBH were used for diluting the tributylphosphate), it was precipitated as acridine nitrate by adding an excess of a solution of acridine in CCl_4. The precipitate was filtered off through a No. 3 or No. 4 crucible, washed with carbon tetrachloride, dried at 90°, and weighed.

As a result of these experiments it was established that addition of acridine to acid (with respect to HNO_3) tributylphosphate leads to formation of a sparingly soluble compound whose composition corresponds to the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$. The solubility of this compound decreases with decreasing percentage content of the tribuylphosphate in the inert solvent (CCl_4, SHBH). Thus the solubility in 5% and 2% solutions of tributylphosphate in CCl_4 is 50 and 20 mg/liter respectively, or in terms of nitric acid 13 and 5.2 mg/liter. At the same time acridine nitrate is almost insoluble in carbon tetrachloride not containing tributylphosphate. Its solubility in solutions of tributylphosphate in SHBH is also dependent to a considerable extent on the tributylphosphate concentration. Accordingly, it is desirable to dilute the test solutions with carbon tetrachloride so that the tributylphosphate content of the latter is not higher than 5%, and then precipitate the nitric acid by adding excess of the free base dissolved in CCl_4. Precipitation experiments (Table 2) showed that gravimetric determination of nitric acid is impossible when the extent to which 20% tributylphosphate solutions is saturated with uranyl nitrate is 50-95%, while the nitric acid content is not greater than 0.02M. On the other hand this is connected with the slight solubility of acridine nitrate in tributylphosphate solution, and on the other hand with the entrainment of some uranyl nitrate in the precipitate, which leads to appreciable (up to 30% relative) errors during gravimetric determination of nitric acid as acridine nitrate. Washing the precipitate on the filter with a 2% solution of tributylphosphate containing about 0.03 M HNO_3 does not always produce the desired effect. It was established that reasonable results could be obtained by applying a correction for the uranyl nitrate entrained in the precipitate. In order to do this a known amount of the precipitate (after the first weighing) was transferred from the porous filter to a porcelain crucible, in which it was weighed; the contents of the crucible were then calcined at 850-900°. The amount of uranyl nitrate which was trapped in the precipitate and determined in this way was then subtracted from the result of the original gravimetric determination (see Table 2).

In some instances (low HNO_3 contents in tributylphosphate solutions) nitric acid can be determined photometrically using the yellow color of acridine in solutions of mineral acids for this purpose.

Table 2. Gravimetric Determination of Nitric Acid in 20% Tributylphosphate Solutions by Means of Acridine•

Expt. No.	Extent to which the tributyl-phosphate sol. is sat. with uranyl nitrate %	Amt. of HNO_3 in sol., mg	HNO_3 found, mg	Deviation from true value	Expt. No.	Extent to which the tributyl-phosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3 in sol., mg	HNO_3 found, mg	Deviation from true value
1	0	55,5	55,0	−0,5	10	70	55,5	61,6	+ 6,1
2	0	97,0	96,6	−0,4	11•••	70	55,5	56,4	+ 0,9
3	5	55,5	55,2	−0,3	12••	90	55,5	67,4	+11,9
4••	5	48,5	48,8	+0,3	13•••	90	55,5	57,0	+ 1,5
5	10	25,0	25,3	+0,3	14	90	25 0	31,2	+ 6,2
6••	10	48,5	49,2	+0,7	15•••	90	25,0	23,7	— 1,3
7••	30	55,5	56.8	+1,3	16	95	25,0	30,5	+ 5,5
8	30	55,5	56,1	+0,6	17•••	95	25,0	25,8	+ 0,8
9	40	55,5	56,2	+0,7					

•The volumes of the original solutions did not exceed 10 ml.

•• 20% Solutions of tributylphosphate in SHBH, the remainder in CCl_4.

••• Corrections applied for uranyl nitrate content as a result of gravimetric determinations.

Just as in the case of gravimetric determination, the precipitate on the filter must be washed with a 2% solution of tributylphosphate in CCl_4 containing a small amount of nitric acid, about 0.03 N; subsequently the precipitate is washed with small portions (5-10 ml) of carbon tetrachloride to remove tributylphosphate, and the acridine nitrate then dissolved in 0.1 N HCl. A calibration curve is constructed by using specially prepared soltuions of tributylphosphate with known nitric acid contents; in this way it is also possible to automatically apply corrections for the slight but definite solubility of acridine nitrate in tributylphosphate solutions. The optical density is measured using a blue filter. Since the solutions do not conform to Beer's law over the working part of the calibration curve, a sufficiently large number of points must be taken. Results of photometric determination are given in Table 3.

Table 3. Photometric Determination of HNO_3 on the Basis of the Color of Acridine Nitrate in 0.1 N HCl.

Expt. No.	Extent to which the tributyl-phosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3, mg	Amt. of test sol., ml	HNO_3 found, mg	Exptl. error (relative)	Expt. No.	Extent to which the tributyl-phosphate sol. is sat. with uranyl nitrate, %	Amt. of HNO_3, mg	Amt. of test sol., ml	HNO_3 found, mg	Exptl. error (relative)
1	0	11,6	2	11,7	+1	9	60	5,8	10	5,8	0
2•	0	11,6	4	11,4	−2	10•	25	5,8	10	5,6	−3
3	50	11,6	2	11,6	0	11	0	5,8	20	6,0	+3
4	50	11,6	2	11,4	−2	12	20	5,8	20	5,9	+2
5	75	11,6	4	11,6	0	13	60	5,8	20	5,6	−3
6•	80	11,6	4	12,2	+5	14	0	1,16	10	1,07	−8
7	0	5,8	10	5,7	−2	15•	5	1,16	10	1,14	−2
8•	5	5,8	10	5,8	0	16	95	1,16	10	1,07	−8

•20% Solutions of tributylphosphate in SHBH, the remainder in CCl_4.

Even smaller amounts of nitric acid (of the order of 0.002-0.0002 M) could obviously be determined nephelometrically directly in tributylphosphate solutions in the presence of uranyl nitrate.

Formation of acridine nitrate is particularly convenient for the qualitative detection of free nitric acid; the limiting dilution is 1:80,000 for 20% solutions of tributylphosphate in SHBH, while the limit of identification is 50 μg. Using this reaction it is possible to detect complex formation (mono- and dialkylphosphates, β-diketones, etc) and solvolysis processes (carboxylic and other organic acids) which occur in tributylphosphate solutions between uranyl nitrate and the compounds indicated, since nitric acid is formed as the result of chemical interaction.

SUMMARY

A new method has been developed for the gravimetric and photometric determination of free nitric acid in tributylphosphate solutions containing varying amounts of uranyl nitrate.

The composition of the compound formed as the result of the interaction of nitric acid and acridine in tributylphosphate solutions corresponds to the formula $C_6H_4 \cdot CH \cdot C_6H_4N \cdot HNO_3$.

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ELEMENTAL ANALYSIS BY THE "WET COMBUSION" METHOD

COMMUNICATION 3. DETERMINATION OF CARBON AND NITROGEN IN NITRO COMPOUNDS ON ONE ALIQUOT*

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The "reduced" and "oxidized" forms of nitrogen can be distinguished by their behavior during the oxidation of nitrogen-containing materials. Amines, imines, etc, which liberate ammonia on oxidation with sulfuric acid, contain the reduced form of nitrogen. Materials with azo-, hydrazo-, nitro- and nitroso groups etc, which, on oxidation, liberate nitrogen as the elemental form or nitrogen oxides, can be regarded as compounds which contain the oxidized form of nitrogen.

Determination of Carbon and Nitrogen in Compounds Containing the Oxidized Form of Nitrogen, Using One Aliquot

Test Material	C, %		Difference	N, %		Difference
	Found	Calculated		Found	Calculated	
2-Methyl-3-carbethoxy-4-nitro-5-methoxy-6-methylbenzofurane $C_{14}H_{15}O_6N$	57,15 57,44	57,33	—0,18 +0,11	4,75 4,58	4,78	—0,03 —0,20
2-p-Nitrophenyl-3-carbethoxy-5-methoxybenzofurane $C_{18}H_{15}O_6N$	63,31 63,39	63,34	—0,03 +0,05	3,90 3,93	4,10	—0,20 —0,17
3,5-Dinitrobenzoic acid $C_7H_4O_6N_2$	39,51 39,71	39,63	—0,12 +0,08	13,22 13,09	13,21	—0,01 —0,12
m-Nitrophenol $C_6H_5O_3N$	51,62 51,57	51,80	—0,18 —0,23	9,89 9,93	10,07	—0,18 —0,14
m-Nitroaniline $C_6H_6O_2N_2$	52,02 51,95	52,17	—0,15 —0,22	20,18 20,31	20,28	—0,10 +0,03
p-Aminoazobenzene $C_{12}H_{11}N_3$	72,82 73,11	73,07	—0,25 +0,04	21,62 21,57	21,31	+0,31 +0,26

Methods have been published for the simultaneous determination of carbon and nitrogen by wet combustion. As a rule, they are suitable for compounds in which the nitrogen is in the reduced form [1-3].

We have shown earlier [4] that during combustion of amines, nitriles, indoles, and pyrrolidines with a mixture of sulfuric and chromic acids, carbon is oxidized to carbon dioxide and can be determined gravimetrically, while nitrogen is converted into ammonium sulfate and can be determined as ammonia by distillation after addition of excess alkali. It has also been found that when the reduced and oxidized forms of nitrogen are present at the same time, only the first of these forms is determined.

The wet combustion method, like the Kjeldahl method, without preliminary reduction, is not suitable for the determination of nitrogen in many organic materials. In order to extend the field of application of Kjeldahl's method, various methods have been suggested for the preliminary reduction of materials containing nitrogen in the oxidized form. The following are examples of materials which have been used as reducing materials: glucose [5], hydrogen

* For communication 2, see Zh. analit. khimii 16, 83 (1961)

iodide [6], thiosalicylic acid [7], chromium chloride [8], a hydrochloric acid solution of stannous chloride [9], zinc dust, etc.

In the work described here we have established that the most suitable reducing agent for preliminary reduction of nitro groups is zinc dust in an aqueous solution of sulfuric acid. It was established that in this way it is possible to determine carbon and nitrogen on one aliquot.

Experimental Procedure. A 50-70 mg aliquot was dissolved in 5 ml of dilute (1:2) sulfuric acid, 0.2 g of zinc dust was added and the mixture heated for 10 min at 100°. During this stage nitro groups were reduced and most of the water was removed by evaporation. When the test material did not dissolve in sulfuric acid, the mixture was carefully stirred so that none of the material was lost on the vessel walls. The flask was then cooled and a further 5 ml of concentrated sulfuric acid added; this was followed by 1.5-2 ml of chromic acid and combustion carried out by the method described earlier [4]. The carbon content was determined from the weight of absorbed carbon dioxide in the tube containing askarite. In order to determine the nitrogen, the sulfuric acid solution remaining after combustion was transferred to a flask fitted with a splash head, 50 ml of 40% potassium hydroxide solution was added, and ammonia distilled as usual into 0.1 N acid solution, excess of which was titrated with 0.1 N alkali in the presence of 2-3 drops of methyl red.

The table contains results for the determination of carbon and nitrogen in a few of the materials analyzed, using one aliquot.

The results obtained show that the "wet combustion" method coupled with preliminary reduction is suitable for the analysis of carbon and nitrogen in nitro compounds. It should be pointed out, however, that this method is not suitable, when, during the reduction process, CO or CS_2 is liberated or acetic acid and other volatile organic materials are formed.

It might be expected that azo compounds should be reduced under the conditions indicated, and that on subsequent combustion it should be possible to determine carbon and nitrogen. Analysis of p-aminoazobenzene showed that in fact the results obtained are close to the theoretical values (see table). It is not likely that hydrazones, which are hydrolyzed in acid media with formation of hydrazine salts, can be analyzed in this way.

When the reduced and oxidized forms of nitrogen are present simultaneously, the suggested method could be used for their separate determination. By carrying out combustion after preliminary reduction the total nitrogen content would be determined, e.g., in p-aminobenzene and m-nitroaniline (see table). By carrying out another combustion without preliminary reduction, only the reduced form of nitrogen would be determined [4]; the oxidized form of nitrogen would then be given by the difference in the two determinations.

SUMMARY

A method has been developed for the determination of carbon and nitrogen in nitro compounds, using one aliquot; it is based on reduction of the nitro group with zinc dust in dilute sulfuric acid, and subsequent wet combustion with chromic and sulfuric acids by a method described earlier. It has been shown that when the reduced and oxidized forms of nitrogen ($-NO_2$ or $-N=N-$) are present simultaneously, the method can be used for their separate determination.

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FLASH COMBUSTION DURING MICRODETERMINATION OF CARBON AND HYDROGEN IN A RAPID STREAM OF OXYGEN

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We have shown earlier that when test material is decomposed in a tube, the decomposition does not proceed simultaneously throughout the whole mass of test material, but layer by layer, and is accompanied by formation of active fragments of the molecules of the test material [1]. The active products from the decomposition are oxidized in the tube and at the exit from the tube. It is the decomposition products of the test material that pass into the oxidation zone, not the vapors of the material. During decomposition in an empty tube and in a rapid stream of oxygen one cannot on any account leave out the zone of preliminary thermal decomposition. Actually if one examines the various methods used for determination of carbon and hydrogen (Table 1), it becomes clear that combustion with slow evaporation (from a boat) can only be carried out by using excess oxygen, when no other oxidizing agent or catalysts are used, while on carrying out combustion with preliminary decomposition (in a test tube within the combustion tube) reliable results can always be obtained without any supplementary filling of the oxidizing zone.

Table 1

Method	Combustion	Whether the oxidizing zone is packed with oxidizing agents and catalysts	Oxygen flow rate, ml/min
Pregl	In a boat	Yes	4
Niederl and Niederl	"	"	4
Friedrich	In a test tube	"	4
Fedoseeva and Pavlenko	In a boat	"	50
Korbl	"	"	50
Belcher and Spooner*	"	No	50
Belcher and Ingram**	"	"	50
Zabrodina	In a test tube	"	30–50
Korshun and Klimova	"	"	30–50

*The method is not universal.
**The oxidizing zone is lengthened and quartz inserted in it.

In addition, it is known that decomposition in a test tube with preliminary pyrolysis has justified itself, whatever gas stream is used: oxygen [2], hydrogen [3], carbon dioxide [4], and nitrogen [5]. In the first two cases the decomposition can proceed with and without participation of the gas, while nitrogen does not participate, and CO_2 can participate in the decomposition process only by virtue of the fact that at high temperatures it partially dissociates into CO and O_2, i.e., the interaction of the gas—in which the decomposition is carried out—with the test material differs in the cases considered. Consequently, the gas in which the decomposition is carried out does not play a decisive role when determinations are made in a rapid stream. A common feature of all the analytical methods involving a rapid gas stream is that decomposition proceeds at the same rate as in the test tube, which behaves as a semisealed zone, from which the gas stream cannot carry out with it the vapors of the test material and the inactive decomposition products. We should like to emphasize that the time for which the vapor of the test material is in contact with the hot surface of the test tube walls and with the hot gas is determined, not by the fas flow rate, as inevitably occurs during evaporation from a boat, but by the analyst, who by carefully following the decomposition can carry out the process at faster or slower rates depending on the properties of the test compound.

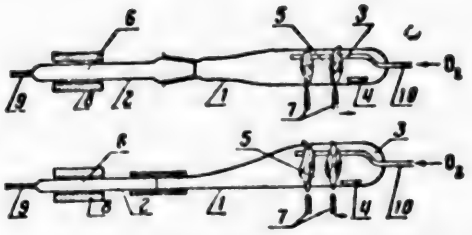


Fig. 1. Tube for highspeed combustion with a ground joint (above) and rubber fitting (below). 1) First part of the tube from the test tube l = 130 mm, d = 15-17 mm; 2) second part of the tube l = 160 mm, d = 5 mm; 3) outlet (l = 80 mm, d = 2 mm), along which the oxygen passes; 4) sample aliquot; 5) decomposition zone; 6) oxidation zone; 7) burner; 8) oven (l = 110 mm) at 950°; 9) end of tube to which the absorption apparatus is connected; 10) outlet (l = 60 mm, d = 2 mm) which is connected to the oxygen supply system.

Complete thermal decomposition can be regarded as a three stage process:

1. Decomposition of the material in the solid or liquid phase with formation of gaseous products, during which the compound either preserves its structure, or the molecule breaks down with formation of fragments with low activity.

2. Decomposition of the material in the gaseous phase with formation of active fragments.

3. Oxidation, hydrogenation, or some other destructive breakdown of the active molecules; this last process always proceeds very rapidly.

Decomposition of the test material in the solid or liquid phase is a direct function of the heating rate, which is controlled by the analyst so that the decomposition only occurs inside the semisealed zone. Since the dimensions of the test tube do not guarantee decomposition of the whole mass of sample all at once, the process must be carried out gradually, and its rate limited by the capacity of the test tube. The rate can only be increased in those cases where the volume of the semisealed decomposition is increased. Subsequent decomposition of test material depends not so much on the rate of heating as on the temperature. In a large semisealed zone the active fragments of the compound can react further. This last process occurs so rapidly in oxygen that it is almost complete inside the decomposition zone and it is the final combustion products that pass almost completely into the oxidation zone.

On the basis of what has been said above, we have developed a rapid and simple method for carbon and hydrogen determination. In this design we retained the semisealed zone, but increased its size so that combustion could be carried out as fast as possible. Since the test tube had been increased in size, that of the combustion tube could not be increased, since an increase in the size of the latter would affect the purging time; its design, therefore, had to be modified. By connecting the test tube, in which decomposition was carried out with the combustion tube into one unit (Fig. 1), we were able to increase the decomposition zone appreciably and at the same time only alter the total volume of the combustion tube to a small extent. As we established, combustion can be carried out very rapidly (in 2-3 min) in such an apparatus, without need for control on the part of the analyst.

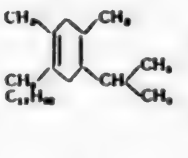
The principle of the highspeed combustion method we have developed consists in rapid combustion of test material in a large semisealed decomposition zone in a rapid stream of oxygen. Oxidation products are absorbed and determined as usual. The method has also proved suitable for analyzing compounds with angular methyl groups; such compounds are known to be the most difficult to analyze.

EXPERIMENTAL

Experimental Procedure. Analysis is carried out in the usual apparatus used for rapid determination of carbon and hydrogen. The combustion tube is made from transparent quartz and consists of two parts connected together either via a ground joint (Fig. 1) or joint to joint covered with rubber. (Fig. 1). The oxygen passes into the first part of the tube through an 80 mm long quartz capillary fused internally and bent toward the wall. This capillary is a continuation of the outlet which connects the tube with the oxygen purifying system. The tube itself is wider than the usual tubes and is constricted toward the point at which it is connected to the second part. The second part of the tube is straight, is 200-280 mm long and has an internal diameter of 7 mm. The end of the tube is drawn out as usual and is connected to the absorption apparatus. A 3-10 mg aliquot contained in a boat or in a quartz capillary is placed in the sealed end of the tube, which acts as a semisealed decomposition zone (the open end of the capillary containing an aliquot should reach the bottom of the tube). An electric oven 70-110 mm long (oxidation zone) heated to 950° is fitted on the second part of the tube. Both parts of the tube are connected and combustion commenced. Combustion is carried out with two burners. One (the stationary one) burner is fixed at the point at which the oxygen enters the apparatus, while the second (the movable one) burner is moved away from the first toward the sealed end of the tube. The material flashes and burns. Combustion takes 2-3 min. Very rarely, only in the case of materials

Table 2

Test material	C, %			H, %		
	Found	Calculated	Difference	Found	Calculated	Difference
I	88,50	88,68	0,16	13,36	13,33	+0,03
	88,64		−0,02	13,34		+0,01
II	71,16	71,02	+0,14	7,91	7,95	−0,04
	71,23		+0,21	7,93		−0,02
III	78,13	78,23	−0,10	6,98	6,88	+0,08
	78,12		−0,11	6,90		−0,02
IV	59,85	59,57	+0,28	6,57	6,43	+0,15
	59,87		+0,30	6,54		+0,11
V	58,05	58,17	−0,12	5,78	5,49	−0,29
	58,06		−0,11	5,76		−0,27
VI	52,58	52,74	−0,18	5,55	5,53	+0,02
	52,60		−0,14	5,63		+0,10
VII	77,93	78,01	−0,08	9,08	9,00	+0,08
	78,13		+0,12	9,13		+0,13
VIII	70,96	71,02	−0,06	7,94	7,95	−0,01
	70,94		−0,08	7,86		−0,09
IX	84,92	84,87	+0,05	14,92	15,13	−0,21
	84,98		+0,11	15,00		−0,13
X	65,86	65,91	−0,05	7,74	7,74	0,00
	65,87		−0,04	7,82		+0,08
XI	57,12	57,13	−0,01	6,07	6,16	−0,09
	57,10		+0,05	6,26		+0,10
XII	93,72	93,68	+0,04	6,32	6,32	0,00
	93,60		−0,08	6,42		+0,10



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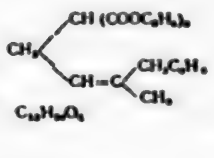

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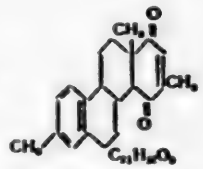

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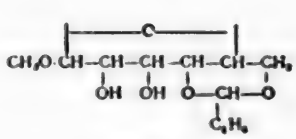

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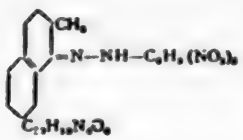

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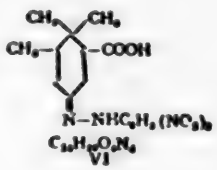

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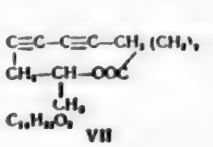

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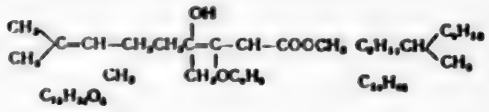

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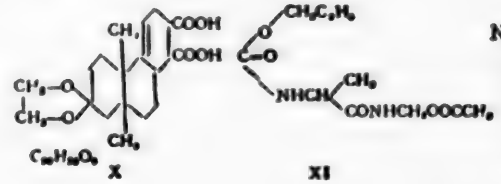

X XI XII

Naphthalene $C_{10}H_8$

6*

which are difficult to burn, is it necessary after 2 min to move the burner away for 1-2 min in order to let in a fresh lot of oxygen into the decomposition zone; this operation is repeated after heating for 2-3 min. Combustion proceeds so rapidly that in practice there is no need for supervision. 250-300 ml of oxygen is used for clearing out the combustion products, i.e., only 7-10 min. Thus the longest part of the analysis is the weighing operation. Twelve carbon and hydrogen determinations can be carried out in a six-hour working day.

Table 2 contains results for some compounds.

SUMMARY

Emphasis is laid on the importance of the semisealed decomposition zone for quantitative decomposition of organic compounds in a gas stream. It has been shown that the time required for complete decomposition of a sample of test material is shorter, the larger the size of the decomposition zone. A new method for the combustion of organic compounds has been developed for the microdetermination of C and H. When this technique is used decomposition in a large semisealed zone is complete within 2-3 min and does not require supervision on the part of the analyst. The accuracy of the method is ± 0.3%.

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A RAPID MICROMETHOD FOR THE DETERMINATION OF FLUORINE IN MONOMERIC AND POLYMERIC FLUOROORGANIC COMPOUNDS

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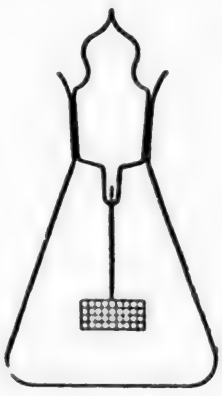
Institute of High Molecular Weight Compounds, Academy of Sciences,
USSR, Leningrad
pp. 469-471, July - August 1961
Original Article submitted September 12, 1960

Various micromethods have been published for the determination of fluroine in fluoroorganic compounds [1-15]. Schoniger's simple and rapid method [16] suited our purpose best. We carried out combustion of fluoroorganic compounds in a closed flask filled with oxygen (diagram), the gaseous products formed being absorbed with twice-distilled water. Instead of titrating with cerium chloride in the presence of murexide, we determined fluoride ions by direct titration with thorium nitrate, using sodium alizarinsulfonate as indicator. The normality of the $Th(NO_3)_4$ was determined by means of pure fluoracetamide; this technique eliminates the necessity of applying a correction during determination of the fluorine content (only a blank test is carried out). The titration is carried out in the same flask as that used for combustion. The results given in Table 1 show that the error does not exceed ±0.3%.



Combustion flask.

The percentage content of fluorine in polymeric compounds was determined by two methods.

1. By the method suggested by Gel'man et al [14] for the simultaneous determination of carbon, hydrogen, and fluorine, in which the magnesium fluoride is subsequently pyrohydrolyzed and a calibration curve is used; all the corrections recommended by the author were applied.

2. By the method suggested above, which does not involve the use of a calibration curve, and only a blank is taken into account.

For fluorine contents less than 60% the solution being titrated was diluted with water to a constant volume of 50 ml; for higher fluorine contents the volume was made up to 100 ml. 3-7 mg aliquots were used.

In the case of high fluorine contents, and in the absence of hydrogen in the fluoroorganic compound, a small amount of pure paraffin (about 3-5 mg) was added to the test aliquot before combustion in order to ensure complete decomposition. 12-16 determinations can be carried out in a 6 hr working day.

Determination of Fluorine. An aliquot of fluoroorganic compound (3-7 mg) was wrapped up in filter paper and ignited in a platinum grid in a 250 ml flask with a standard ground joint (see diagram). Ten ml of twice-distilled water had been introduced into the flask beforehand. The contents of the flask were shaken for 3-5 min until the vapour cloud had disappeared. The experimental technique has been described earlier [17]. The flask was opened and the volume of liquid made up to 50 ml. 0.6 ml of 1% alizarin red S was added. The solution was neutralized with 0.1 N NaOH until the solution had a red color; 1-2 drops of 0.025 N HNO_3 was then added until a yellow colored developed. In order to establish the requisite pH (2.9-3.00) 3.5 ml of buffer mixture (1 N $CH_2ClCOOH$ + 1 N NaOH; 1:1) was added. The whole sample was titrated in the same flask with 0.025 N $Th(NO_3)_4$. The volume of $Th(NO_3)_4$ used up for titrating the blank (about 0.04 ml) was subtracted from the volume of titrant used for titrating the sample. The blank was carried out under the same conditions but without a sample.

The normality of the $Th(NO_3)_4$ solution was established by means of aliquots (3-5 mg) of pure fluoroacetamide dried to constant weight at 55-60°.

Table 1

Test Material	Sample wt, mg	Fluorine content % Found	Fluorine content % Cal.	Difference
Fluoroacetamide C_2H_4FNO	3,670	24,57	24,66	—0,09
	3,925	24,54		—0,12
Benzotrifluoride $C_7H_5F_3$	2,595	38,99	39,01	—0,02
	3,220	38,88		—0,13
Mono-β-trifluoroethylamidemaleic acid*. $C_6H_6F_3NO_3$	5,155	28,62	28,92	—0,30
	5,915	28,81		—0,11
Mono-β-trifluoroethylamidecitraconic acid* $C_7H_8F_3NO_3$	2,875	26,74	27,00	—0,26
	3,000	27,00		±0,00
ϕ-Fluoroamylmethacryclate of $C_9H_8F_8O_2$	4,107	50,74	50,64	+0,10
	6,258	50,72		+0,08
2,4-Dinitrophenylhydrazone-1,1,1-trifluoroacetone $C_9H_7F_3N_4O_4$	5,675	19,21	19,50	—0,29
	7,320	19,33		
Trifluoromethylphenylmethacrylamide $C_{11}H_{10}F_3NO$	2,660	24,87	24,87	—0,17
	2,710	24,95		±0,00
Tenoyltrifluoroacetone $C_8H_5F_3O_2S$	6,185	25,53	25,65	+0,08
	4,995	25,44		—0,12
				—0,21
Mixture of fluoroacetamide and tetrachlorophthalic anhydride $C_2H_4FNO + C_8Cl_4O_3$	2,840			
	+4,110	24,82		+0,16
	+3,410		24,66	0,24
	3,715	24,90		
Mixture of fluoroacetamide and thiocyanochloro $C_2H_4FNO + C_7H_4ClNS$	3,350	24,60	24,66	—0,06
	+3,680			
Mixture of tenoyltrifluoroacetone and tetrachlorophthalic anhydride $C_8H_5F_3O_2S + C_8Cl_4O_3$	3,795			
	+3,860	25,38	25,65	—0,27
	4,580	25,47		—0,18
	+3,365			

*These samples were synthesized by T. V. Sheremetova, Z. V. Borisova, and V. V. Kudryavtsev.

Table 2

Test Material	F found, % By pyrohydrolysis with MgO	F found, % By combustion in a flask
Polytetrafluorethylene $(-C_2F_4^-)^n$	75.98*	76.08
		75.74
Polymer 1**	8.83	8.87
	8.77	9.09
Polymer 2	10.61	10.48
		10.33
Polymer 3	19.73	19.61
	19.74	19.83
Polymer 4	33.38	33.21
	33.26	33.30

*The theoretical fluorine content is given for Teflon

**These polymers were synthesized at the Institute of High Molecular Weight Compounds, Academy of Sciences, USSR.

SUMMARY

A rapid micromethod is suggested for the determination of fluorine in monomeric and polymeric fluoroorganic compounds. The determination is carried out by combustion of an aliquot of test material in a flask filled with oxygen, followed by absorption of the combustion products with twice-distilled water, and titration of hydrofluoric acid with 0.025 N $Th(NO_3)_4$, using alizarin red S.

A small amount of pure paraffin (3-5 mg) is added to fluoroorganic compounds which do not contain hydrogen in order to ensure their complete decomposition.

The method is rapid, the apparatus is simple, and there is no need to transfer the absorption liquid into another vessel. Nitrogen, sulfur, and chlorine do not interfere with the determination. The experimental error is ± 0.3%. One determination takes 20-25 min.

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SIMULTANEOUS DETERMINATION OF FLUORINE, SILICON, AND CHLORINE IN SILICOORGANIC COMPOUNDS CONTAINING FLOURINE AND CHLORINE

E. A. Bendarevskaya, V. M. Kuznetsova, and S. V. Syavtsillo

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pp 472-476, July-August, 1961
Original Article submitted June 14, 1960

Series of articles are being published at present on the development of methods for the determination of fluorine [1-7], the simultaneous determination of carbon and fluorine [8,9], simultaneous determination of carbon, hydrogen, and fluorine [10-15], fluorine and nitrogen [16], and silicon [17] in compounds of the type $H(CF_2CF_2)_xSiCl_3$. There are no published methods on the simultaneous determination of silicon, chlorine, and fluorine in fluorochlorosilicoorganic compounds.

Table 1

Test Material	Sample wt.,mg	Found %		Deviation from the theoretical value %	
		F	Si	F	Si
$(CF_2CH_2CH_2)_2Si(OC_2H_5)_2$*	25,684	39,7	7,5	—0,9	—0,4
Calculated 40,6% F; 7,9% Si	20,901	39,9	7,8	—0,7	—0,1
$CF_2CH_2CH_2(CH_3)Si(OC_2H_5)_2$*	35,433	24,5	12,6	—0,3	+0,4
Calculated 24,8% F; 12,2% Si	20,001	24,9	12,1	+0,1	—0,1
$F_2C_6H_3(CH_3)Si(OC_2H_5)_2$	15,018	15,9	11,6	+0,5	+0,2
Calculated 15,4% F; 11,4% Si	18,990	15,1	11,9	—0,3	+0,5
$FC_6H_4(CH_3)Si(OC_2H_5)_2$	31,221	8,2	12,8	—0,1	+0,5
Calculated 8,3% F; 12,3% Si	18,426	7,9	12,5	—0,4	+0,2

* A.L. Klebanskii prepared the pure materials which he kindly gave us to develop the method.

Table 2

Test Material	Sample wt.,mg	Found %		Deviation from the theoretical value,%	
		F	Si	F	Si
Polymer № 1	44,310	23,0	20,9	+0,4	+0,1
Calculated 22,6% F; 20,8% Si	50,080	22,8	21,4	+0,2	+0,5
Polymer № 2	40,349	35,9	17,7	+0,5	—0,2
Calculated 36,5% F; 17,9% Si	56,384	36,7	17,4	+0,2	—0,5
Polymer № 3	28,911	22,2	14,8	+0,4	+0,5
Calculated 21,8% F; 14,3% Si	47,876	22,4	14,7	+0,6	+0,4

During a study of a method for determining fluorine in organic compounds [1] which is applicable to fluorine-containing silicoorganic materials, we established that it is possible to determine fluorine, chlorine, and silicon simultaneously.

Essentially, the cited method of determining fluorine [1] consists in fusing an aliquot of the fluoroorganic compound with potassium metal in a steel bomb at 800-850° for 10-15 min. The melt obtained is dissolved in water, and fluoride is determined in an aliquot of the solution by titration with thorium nitrate. The authors have examined the possibility of determining fluorine in the presence of chlorine, sulfur, nitrogen, and phosphorus.

Table 3

Test Material	Sample wt.,mg	Decomposed for 45 min at 950°		Decomposed for one hour at 1000°	
		F	Si	F	Si
$(CH_3)(C_6H_5F_3)_2SiCl$	30,355	18,1	9,7		
	32,046	19,4	10,0		
Calculated 25,0% F; 9,5% Si	31,848			17,5	10,2
	29,001			18,8	9,9
Polymer № 4	38,222	16,4	14,8		
	40,081	16,0	14,6		
Calculated 23,0% F; 14,6% Si	25,016			17,0	14,7
	39,495			16,6	14,9

Table 4

Test Material	Sample wt.,mg	Decomp. in oxygen atmosphere 45 min 1000		60 min 1000°	
		F	Si	F	Si
$(CH_3)(C_6H_5F_3)_2SiCl$	39,392	19,2	10,1		
	37,455	19,9	10,1		
Calculated 25,0% F; 9,5% Si	41,040			25,4	10,1
	23,000			25,4	9,8
Polymer № 4	27,961	16,8	14,7		
	29,351	16,5	14,4		
Calculated 23,0% F; 14,6% Si	28,931			23,3	14,5
	32,466			22,9	14,7
$(F_2C_6H_3)_2(CH_3)Si(OC_2H_5)$	28,606			24,7	8,3
Calculated 24,2% F; 8,9% Si	20,333			24,1	8,0

Silicon can be determined titrimetrically by the hydroxyquinoline and acidimetric methods. The first method, which is based on formation of a sparingly soluble silicomolybdate hydroxyquinoline complex [18-20], has not found wide application. Stobba [21] was the first to suggest the acidimetric method, and it was subsequently improved and modified by many workers [22-27]. The simplest and most reliable variant of this method is based on formation of ammonium silicofluorosilicate in the presence of hydrochloric acid. The silicon content is determined from the amount of hydrochloric acid which participates in the reaction, i.e., the determination reduces to titration of excess acid with alkali [27]. $Si(OH)_4 + 6NH_4F + 4HCl = (NH_4)_2SiF_6 + 4H_4Cl + 4H2O$. In order to avoid side reactions of fluorine with glass, and also of glass with alkali, we used gelatin capsules or polyethylene ampoules for holding the samples. We made the latter from polyethylene tubing of suitable diameter.

The method was developed using individual monomeric silicofluoroorganic compounds, whose carbon and hydrogen contents, refractive index, specific gravity, and molecular refraction corresponded to those of the chemically pure materials*.

The experimental results obtained showed that the time required to decompose some silicoorganic compounds containing fluorine is 45 min at 900-950°. The color change at the end point was not clearly defined on titrating with 0.01 N KOH, and variable results were obtained for silicon, mainly results on the low side. Accordingly, in our subsequent experiments we determined silicon by titrating the acid with 0.1 N alkali solution.

Table 1 contains the results obtained during simultaneous determination of F and Si in individual monomeric silicofluoroorganic compounds containing one or two fluorine atoms on one phenyl or alkyl radical.

Analysis of pure polymeric silicoorganic compounds containing fluorine in the aliphatic radicals showed that it should be possible to determine fluorine and silicon simultaneously in these compounds with reasonable accuracy (Table 2).

*K.F. Grinevich made the chemically pure materials, which he kindly gave us to develop the method.

Table 5

Test Material	Sample wt. mg	Found %			Deviation from the theoretical value %		
		F	Si	Cl	F	Si	Cl
$(C_2H_3)(CH_3)(C_6H_3F_2)SiCl$	26,843	16,9	12,6	15,7	—0,2	0	—0,4
Calculated 17,1% F; 12,6% Si; 16,1% Cl	27,498	17,0	12,6	15,9	—0,1	0	—0,2
$(F_5C_6H_5)(CH_3)SiCl_2$	42,659	17,5	13,2	30,9	+0,5	+0,6	0
Calculated 17,0% F; 12,5% Si; 30,9% Cl	26,688	17,4	12,9	30,8	+0,4	+0,4	—0,1
$(C_6H_4F)(CH_3)SiCl_2$	19,173	9,5	13,5	34,1	+0,4	—0,1	+0,1
Calculated 9,1% F; 13,6% Si; 34,0% Cl	12,286	9,2	13,2	33,9	+0,1	—0,4	—0,1
$(CF_3CH_2CH_2)_2SiCl_2$	35,117	39,2	8,9	24,2	+0,3	—0,1	0
Calculated 38,9% F; 9,0% Si; 24,2% Cl	35,712	39,0	8,7	24,4	+0,1	—0,3	+0,2

During analysis of monomeric compounds containing two fluorinated phenyl radicals on the silicon atom, and also during analysis of polymeric compounds with fluorinated phenyl radicals, it was observed that the radicals were split off and that they were incompletely decomposed; accordingly, the silicon was determined quantitatively, while the fluorine was not completely determined (Table 3).

These results can be explained by the values of the energy of the chemical bonds C – F, and C – Si [28]. In the first instance the energy is 104 kcal/mole, while in the second instance it is only 58 kcal/mole.

By fusing test material with potassium metal in an oxygen filled bomb for 60 min at 1000° we were able to destroy the fluorinated radicals completely. It is obvious that not only reducing but also, to some extent, oxidizing reactions occur during this process.

Results of the determination of fluorine and silicon contents are given in Table 4. Chlorine can be determined at the same time as fluorine and silicon, a thiocyanate titration being used for this purpose (Table 5).

Experimental Procedure. A 20-40 mg aliquot of test material contained in polyethylene ampoules or gelatin capsules is placed in a metal bomb, and fused with 4-5 times its amount of potassium metal. The fusion time and the temperature chosen depend on the nature of the test material. When the test material contains one fluorinated phenyl radical or fluorinated alkyl radicals on the silicon atom, fusion is carried out at 900-950° for 40-45 min. When two or more fluorinated phenyl radicals are present on the silicon atom, fusion time is increased to 60 min, and the temperature increased to 1000°. In the latter instance the bomb is swept with oxygen for 2-3 min before an analysis. After fusion, and after the bomb has been cooled, the latter is opened and excess potassium metal carefully removed by addition of water; the contents of the bomb are then quantitatively transferred to a 200 ml standard flask. Fluorine, chlorine, and silicon are then determined by separate titration of aliquots of this solution.

Fluorine is determined by the method described in [1]. Chlorine is determined by a thiocyanate titration [29].

Silicon Determination. Twenty-five ml of the solution is transferred to a titration flask, 5-6 drops of indicator* is added, and the solution neutralized first with HCl (1:1) and (1:10) until it has a weakly acid reaction, and then neutralized accurately with 0.1 N alkali. During this stage the total volume of solution should not exceed 50 ml. The solution is next saturated with potassium chloride (30-50 mg), and again accurately neutralized with 0.1 N alkali solution and 0.1 N acid 2 ml of a neutral solution of ammonium fluoride** is added followed by 10 ml of 0.1 N

*The indicator is prepared by mixing the following two solutions: a) 0.1% alcoholic solution of methyl red; b) to 100 ml of an aqueous solution of bromocresol green is added 0.5 ml of 0.1 N NaOH. Six parts of solution(a) is mixed with five parts of solution(b).

**40 ml of 25% ammonia is mixed with 25 ml of 40% hydrofluoric acid. This mixture is then diluted to one liter with water, and after a rough neutralization, neutralized accurately using an indicator. The acidity of the solution prepared is checked daily before use. For this purpose 20 ml of 0.1 N HCl and 10 ml of NH_4F are titrated with 0.1 N KOH. If the amount of alkali differs from the amount of the latter used in titrating the pure acid, then the fluroide solution should be neutralized again.

hydrochloric acid, and excess acid titrated rapidly with alkali. The color change at the end point is from red to green. The silicon content is calculated by means of the formula:

$$Si\ \% = \frac{(V - V_0)\,K \cdot 0{,}7015 \cdot 8 \cdot 100}{a},$$

where V is the volume of 0.1 N alkali used in titrating 20 ml of 0.1 N hydrochloric acid *, ml; V_0 is the volume of 0.1 N alkali* used in titrating the acid which has not reacted during formation of ammonium silicofluoride, ml; K is the correction for the normality of the 0.1 N alkali; 0.7015 is the amount in mg of silicon corresponding to 1 ml of 0.1 N hydrochloric acid; a is the sample weight; 8 is the dilution factor.

SUMMARY

A method is suggested for the simultaneous determination of fluorine, silicon, and chlorine in some monomeric and polymeric silicoorganic compounds containing fluorine and chlorine. The accuracy of the method is 0.2-0.5% absolute.

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* The 0.1 N HCl is standardized against potassium iodate using a mixed indicator. The 0.1 N KOH is standardized against the 0.1 N HCl using the same indicator.

POLAROGRAPHIC DETERMINATION OF 2-METHYL-5-VINYLPYRIDINE

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In recent years 2-methyl-5-vinylpyridine has acquired importance as a monomer in the production of synthetic rubbers, and also of various copolymers, including, e.g., copolymers with acrylonitrile and methylmethacrylate (U.S.A. Patent 2688012, Ref. Zh. Khim. 1956, No. 41293) etc. Copolymerization of 2-methyl-5-vinylpyridine with styrene may also be of special importance in certain specific cases. The necessity of determining this monomer quantitatively, particularly during a study of its polymerization (or copolymerization) kinetics, makes it essential to find methods which will enable changes in the amount of this compound in reaction mixtures and also in polymers to be determined rapidly and objectively.

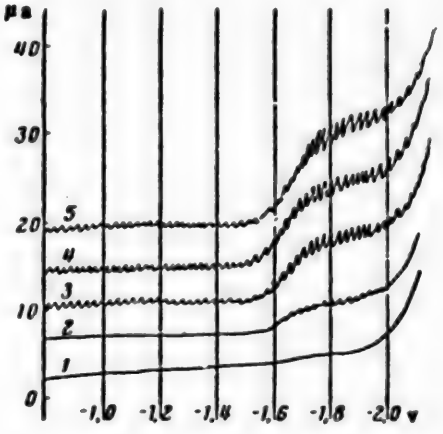


Fig. 1. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a saturated solution of $(CH_3)_4NI$ in 92% CH_3OH against an internal anode (E = − 0.413 v). 1) Supporting electrolyte; 2) 0.034 g/liter; 3) 0.096 g/liter; 4) 0.124 g/liter; 5) 0.151 g/liter.

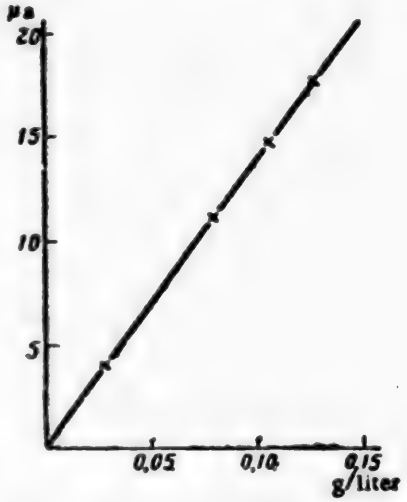


Fig. 2. Calibration curve for methylvinylpyridine in a supporting electrolyte of $(CH_3)_4NI$ in 92% CH_3OH.

The authors' experience in recent years has convinced them that the polarographic method is of definite importance for solving such problems. Although a considerable number of papers have been published which have been devoted to polarographic studies of pyridine and some of its derivatives [1-5], we have not seen any published information on the polarographic behavior of methylvinylpyridine.

In this connection we have carried out a detailed study of the polarographic activity of this compound, and on the basis of the results obtained we have developed methods for its qualitative polarographic determination.

Experimental Procedure. Polarographic measurements were made on a photorecording M-103 polarograph, using a dropping mercury electrode with the following characteristics: m = 2.354 mg/sec, τ = 3.5 sec. (at E = 0). In some instances we also used a Sommer type capillary [6] with τ from 3 to 1.5 sec; nevertheless we cannot recommend this type, because its dropping period is not stable enough.

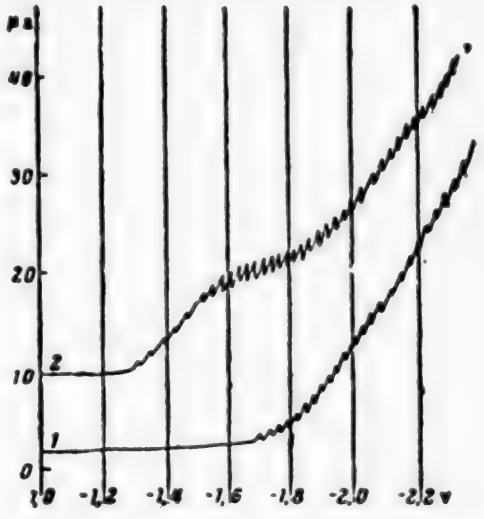


Fig. 3. Polarographic wave for methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 5.85. 1) Supporting electrolyte; 2) 0.307 g/liter.

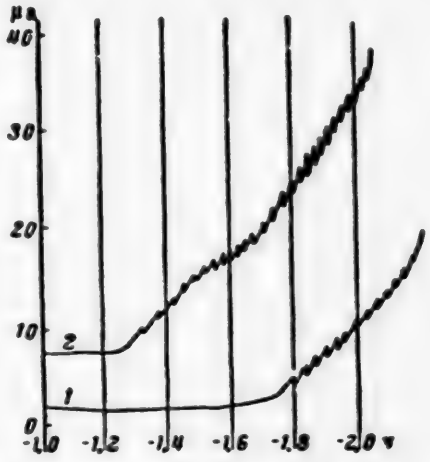


Fig. 4. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 6.45. 1) Supporting electrolyte; 2) 0.079 g/liter.

The following solutions were used as supporting electrolyte: $(CH_3)_4NI$ in 92% CH_3OH (saturated solution); 0.05 N solution of $(CH_3)_4NI$ in 25% CH_3OH; a mixture of 0.05 N $(CH_3)_4NCl$ and $(CH_3)_4NOH$ in 20% CH_3OH. Buffer solutions with pH from 4.7 to 12.2, based on acetic acid, phosphoric acid, phenol, and tetramethylammonium hydroxide were also used.

Analytical grade $AlCl_3 \cdot 6H_2O$ was used for precipitating the polymer.

Solutions of 2-methyl-5-vinylpyridine in methanol with concentrations of 11.508, 1.1508, and 2.2576 g/liter were used as standard solutions.

The 2-methyl-5-vinylpyridine, which was synthesized at the Yaroslavskii Technological Institute, was distilled under vacuum in a nitrogen stream and had the following constants:

$$d^{25} = 0.9564 \text{ g/cm}^3; \; n_D^{20} = 1.5430.$$

Solutions were polarographed in an electrolyzer with an internal anode, and also with an external anode – a saturated calomel electrode. $E_{1/2}$ values are given relative to the potential of the saturated calomel electrode.

Results. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a saturated solution of $(CH_3)_4NI$ in 92% CH_3OH are shown in Fig. 1. $E_{1/2} = -2.08$ v. Waves of methylvinylpyridine in a supporting electrolyte of 0.05 N $(CH_3)_4NI$ in 25% CH_3OH are similar in character; $E_{1/2} = -2.04$ v.

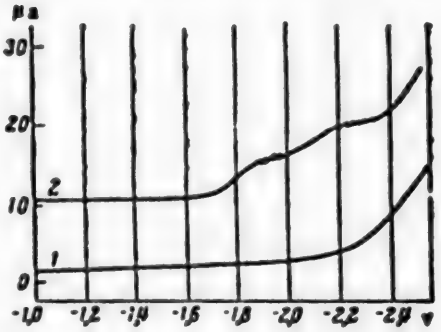


Fig. 5. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 9.74. 1) Supporting electrolyte; 2) 0.152 g/liter.

TABLE 1. Diffusion Current Constants for Methylvinylpyridine in a Supporting Electrolyte of $(CH_3)_4NI$ in 92% CH_3OH

c, mM/liter	I_d, μa	$K = \frac{I_d}{m^{2/3}\tau^{1/6}c}$
0,285	2,80	5,24
0,807	7,885	5,09
1,045	10,368	5,18
1,269	12,513	5,15

TABLE 2. Determination of Methylvinylpyridine in Synthetic Mixtures

Monomer in the polymer, %		Error (relative), %
Taken	Found	
2.78	2.68	−3.6
3.33	3.40	+2.1
11.31	11.40	+0.64
12.24	12.80	+4.6
13.14	13.08	−0.61
14.09	14.16	+0.66

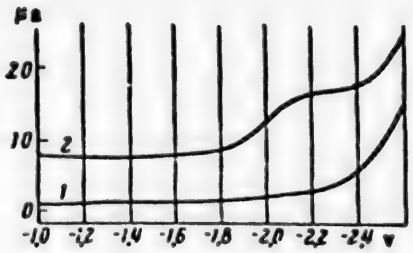


Fig. 6. Polarographic wave of methylvinylpyridine in a supporting electrolyte of a buffer solution with pH 11.65. 1) Supporting electrolyte; 2) 0.153 g/liter.

The value of the diffusion current of methylvinylpyridine is a linear function of its concentration (Fig. 2); this is also confirmed by the constancy of the diffusion current constant at different concentrations of the test material (Table 1).

During a study of the effect of pH on the polarographic indices of 2-methyl-5-vinylpyridine, the results shown in Figs. 3, 4, 5, and 6 were obtained. In the course of this work it was established that one wave with a poorly defined limiting current zone is observed in acid solutions, so that the wave height cannot be measured sufficiently accurately.

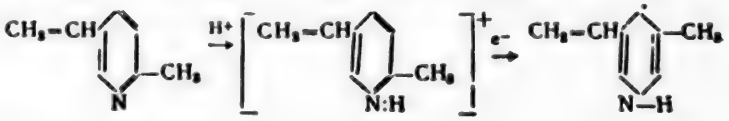
Starting from pH 6 a poorly defined second wave appears which almost coincides with the wave for the supporting electrolyte.

At pH 9.74 both waves become fairly clearly distinguishable, but at pH 11 they fuse together to give one wave with a well defined limiting current zone suitable for polarographic measurements to be carried out. The wave height, as the diagram shows, also varies with pH changes.

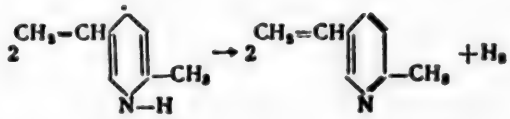
In addition, it was established that the relationship between the wave height of 2-methyl-5-vinylpyridine and its concentration is not linear in acid, neutral, and weakly alkaline solutions up to pH 10. An appreciable drop in the value of the limiting current with increasing pH was observed. On the other hand, the value of the limiting current under these conditions does not depend on the height of the mercury column.

Waves of methylvinylpyridine in alkaline buffer solutions with pH ≥10 are different in character. At these values of the pH of the supporting electrolyte $I_{limiting}$ is proportional to the concentration of the test monomer and changes linearly as a function of $\sqrt{H}$.

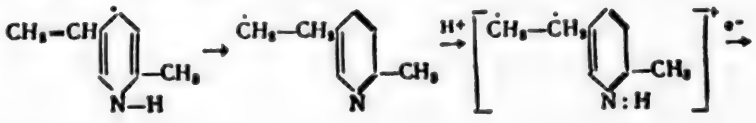
It can be assumed therefore that in acid, neutral, and weakly alkaline buffer solutions (pH <10) the waves are catalytic in nature and that the electrode process corresponding to them can be expressed by the following scheme:

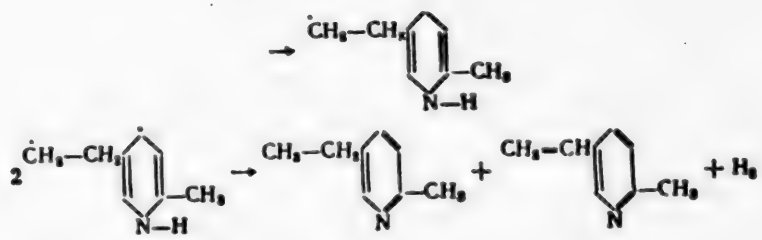


In acid buffer solutions

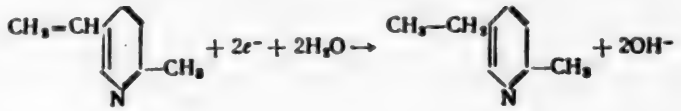


In neutral and weakly alkaline buffer solutions





In alkaline solutions with pH>10 reduction of 2-methyl-5-vinylpyridine is diffusive in character and is expressed by the following scheme:



Quantitative Determination of 2-Methyl-5-Vinylpyridine. Quantitative determination of 2-methyl-5-vinylpyridine in pure solutions does not present any difficulties and can be readily carried out in supporting electrolytes of buffer solutions with pH from 11 upward, both by using a calibration curve, and by the method of additions. It is considerably more difficult to determine this monomer in polymethylvinylpyridine, and also in its copolymer with styrene.

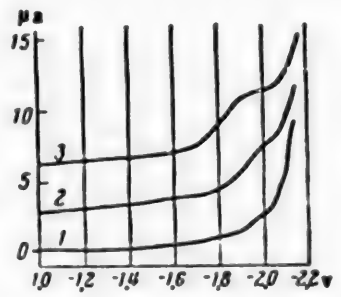


Fig. 7. Polarographic waves of methylvinylpyridine in a supporting electrolyte of a mixture of $(CH_3)_4$ NCl and $(CH_3)_4$ NOH for various concentrations of $(CH_3)_4$ NOH in 20% CH_3OH (filtrate obtained after precipitation of the polymer). 1) Supporting electrolyte; 2) 0.072 g/liter; 3) 0.072 g/liter + 0.011 M $(CH_3)_4NOH$.

In addition to being soluble in such solvents as benzene, dioxane, and chlorinated hydrocarbons, methylvinylpyridine is also soluble in alcohols. Methanol cannot therefore be used as a precipitant for these polymers in the given instance.

When polarograms were taken of methylvinylpyridine in the presence of the polymer in a supporting electrolyte of $(CH_3)_4NI$ in 92% CH_3OH, a distorted wave was obtained for methylvinylpyridine, with a maximum which fused with the reduction wave of the supporting electrolyte, while the galvanometer needle oscillated violently.

In 1:4 and 1:5 methanol-water mixtures, polymethylvinylpyridine gives a stable suspension, the particles of which carry a positive charge. Salting out of the polymer proved to be a very difficult problem. Centrifuging, and filtering through a fine filter (a layer of Al_2O_3, No. 3 and No. 4 glass filters) only led to partial separation of the polymer. The filtrate obtained under these conditions was unsuitable for polarographic purposes. Addition of solutions of salts with both mono- and divalent anions, and also of acids and alkalis, to the suspension, led to either partial or complete peptization of the polymer.

Finally, separation of the polymer from solutions containing the monomer was achieved by coprecipitating it with aluminum hydroxide, by gradual addition of a solution of tetramethylammonium hydroxide to an aqueous methanol suspension of the polymer containing an aluminum salt in the presence of methyl red. The filtrate obtained after removal of the polymer precipitated with the aluminum hydroxide was clear and suitable for polarographic purposes.

The polarographic wave of methylvinylpyridine obtained in this filtrate as a supporting electrolyte was, however, poorly defined (Fig. 7, Curve 2), because the pH of the solution being polarographed was not high enough. By adding a small amount of $(CH_3)_4NOH$ to the filtrate, a polarographic wave was obtained for methylvinylpyridine which was suitable for measurement (Fig. 7, Curve 3).

The method used for determining methylvinylpyridine in its polymer and in its copolymer with styrene reduces to the following. An aliquot of polymer or copolymer (about 0.3 g) is placed in a 25 ml standard flask and is dissolved in 5 ml of dioxane (when the polymer is being analyzed, methanol can also be used for dissolving it). After the sample has dissolved completely the volume is made up to the mark with methanol. Two ml of the solution obtained is trans-

ferred to a 10 ml standard flask, 6 ml of water, 0.3 ml of 1 N $AlCl_3$, and two drops of methyl red are added and 0.4 N $(CH_3)_4NOH$ then added in small portions until the color of the indicator changes to yellow. The volume of the mixture is made up to the mark with water and then filtered into a dry vessel. Three ml of filtrate is transferred to the electrolyzer, 0.2-0.4 ml of 0.4 N $(CH_3)_4NOH$ is added, and after nitrogen has been passed through the solution, polarograms are taken. The methylvinylpyridine content is determined by the method of additions.

It is clear from the results given in Table 2 that there is no appreciable absorption of the monomer by the polymer.

The values obtained during determination of methylvinylpyridine in the same sample were: 2.46, 2.38, 2.56, 2.57, 2.41, 2.59, 2.53, 2.45, 2.54, 2.50 g/liter.

The relative experimental error was determined by statistical treatment of the results obtained, using the formula

$$\varepsilon_{rel.} = \frac{t_\alpha S}{\bar{x}\sqrt{n}} \cdot 100\%,$$

where n is the number of determinations, $\bar{x}$ is the arithmetic mean of n determinations, S is the mean square error of an individual determination calculated by the usual formula, α is the confidence level (reliability) (in the given instance $\alpha = 0.95$), and t_α is a multiplier dependent on n and α (see [7]).

The relative error in our case proved to be 2.1%.

The method which we have developed for the quantitative determination of 2-methyl-5-vinylpyridine has been used for studying its polymerization kinetics.

SUMMARY

A study has been made of the polarographic behavior of 2-methyl-5-vinylpyridine in a supporting electrolyte of $(CH_3)_4NI$ in methanol and aqueous methanol solutions, and also in a supporting electrolyte of buffer solutions with different pH values.

A method has been developed for the determination of methylvinylpyridine in its polymers and in its copolymer with styrene. It is based on separation of the polymer from solutions containing the monomer, by coprecipitating the former with $Al(OH)_3$ and taking polarograms of the filtrate in a supporting electrolyte of $(CH_3)_4NOH$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A POLAROGRAPHIC STUDY OF TEREPHTHALIC AND PARA-TOLUIC ACIDS, THEIR NITRO DERIVATIVES, DIMETHYL TEREPHTHALATE, DIMETHYL NITROTEREPHTHALATE, AND METHYL PARATOLUATE

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Development of polarographic techniques for the determination of terephthalic acid, paratoluic acid, mononitroterephthalic acid, 3-nitroparatoluic acid, dimethyl terephthalate, methyl toluate, and dimethyl nitroterephthalate is of considerable interest both from the point of view of the polarography of organic compounds, and also for production control of the intermediate products obtained during the synthesis of fibers of the lavsan type. Of these compounds only dimethyl terephthalate has been examined polarographically [1-3]. A study has, however, been made of the polarographic behavior of dimethyl terephthalate, but only over a narrow concentration range, since aqueous solutions were used. No success has been achieved in obtaining the polarographic characteristics of terephthalic acid [1,2].

EXPERIMENTAL*

Polarograms were taken on an "Orion" (Hungarian) electronic polarograph. The cell was thermostatted at 25± 0.2°. A mercury pool was used as anode. The half-wave potentials were measured relative to a saturated calomel electrode by means of a potentiometer. Three capillaries with the following characteristics were used $m^{2/3}t^{1/6}1.31^{2/3}$ (I), 1.16 mg sec, (II), and 0.89 $mg^{2/3}sec^{-1/2}$ (III). The characteristics were established by disconnecting the circuit in 0.1 N KCl. Oxygen was removed by means of nitrogen.

Buffer solutions (pH 2-12) prepared according to Britton-Robinson were used.

Twice distilled methanol was used in a series of experiments.

Terephthalic Acid. This acid was prepared by saponifying pure dimethyl terephthalate: m.p. 141-142°, ester number 103. The terephthalic acid obtained distilled at a temperature >300° [4] and had an acid number of 119.6.

The stock solutions of terephthalic acid were prepared in 0.5 N NaOH, followed by neutralization with H_2SO_4 using phenolphthalein as indicator.

It was established that a polarographic wave for terephthalic acid could be obtained in a supporting electrolyte of a buffer solution with pH 4.1-5.2. In order to get more clearly defined polarographic waves it was necessary to add – by analogy with the conditions used for polarographing phthalic acid [5] – 0.05 M $CaCl_2$ (Fig. 1). At pH <4.0 and pH >5, the diffusion current constant of terephthalic acid decreases, this being particularly the case at pH <4.0 (Fig. 2). Formation of a precipitate of terephthalic acid appears to be the reason for this decrease in the latter instance. Precipitation of $Ca_3(PO_4)_2$ makes it difficult to obtain satisfactory waves at pH>5.

Thus the optimum pH range for analytical purposes is 4.4-4.8. The half-wave potential ($E_{1/2}$) over this range, 1.45-1.51 v, linearly increases with increasing pH.

At pH 4.6 the value of i_D is proportional to C over the range 0.1-5.0 mM/liter; the diffusion current constant i_D = 3.70 ± 0.06 μa/mM/liter (capillary I). The relationship between i_D and C is not linear for terephthalic acid concentrations >5.0 mM/liter.

Paratoluic acid does not give a polarographic wave in this supporting electrolyte and does not interfere with de-

* Z.V. Zaitseva and M.P. Los' took part in the experimental work.

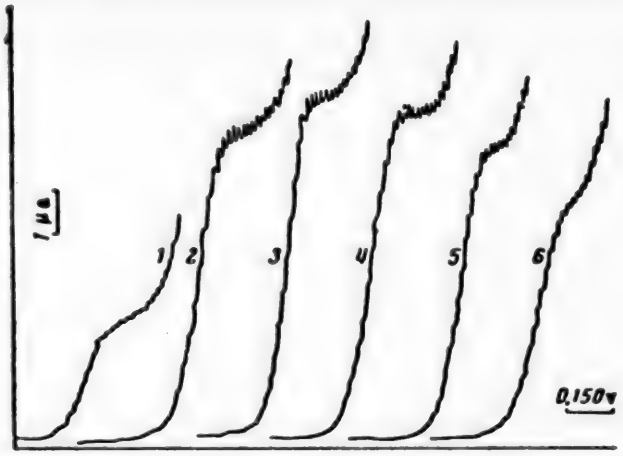

Fig. 1. Polarogram of terephthalic acid at a concentration of 2×10^{-3}M. 1) pH 4.1; 2) pH 4.3; 3) pH 4.6; 4) pH 4.7; 5) pH 5.0; 6) pH 5.2. Initial voltage 1.15 v.

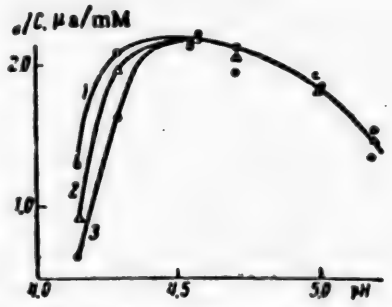

Fig. 2. The relation between the diffusion current constant of terephthalic acid and the pH of the supporting electrolyte. 1) 1.65×10^{-3}M; 2) 1.85×10^{-3}M; 3) 2.5×10^{-3}M.

termination of terephthalic acid.

Nitrate, when present, does not interfere with the polarographic determination of terephthalic acid either.

The polarographic method permits terephthalic acid to be determined in the presence of paratoluic acid and nitric acid. The experimental accuracy, as in the case of the other materials considered below, is not lower than 3-5% (relative).

Paratoluic Acid. This acid was prepared by saponifying methyl paratoluate (m.p. = 32-33°, ester number 66.0). The paratoluic acid has a m.p. of 181-182°, and an acid number of 73.8.

Stock solutions of paratoluic acid were prepared by dissolving the acid in 0.5 N NaOH and then neutralizing.

In a buffering solution, as described above, a polarographic wave for paratoluic acid could not be obtained.

A hydrogen wave with $E_{1/2}$ = 1.57-1.60 v and I_D = 2.6 ± 0.14 μa/mM/liter (capillary III, concentration range 0.1-2 mM/liter) is obtained for solutions of paratoluic acid in a supporting electrolyte of 0.1 N $(CH_3)_4NI$.

In order to determine paratoluic acid we studied the polarographic behavior of its nitration product.

It was established that at low concentrations, paratoluic acid, even at room temperature, is readily nitrated by nitric acid whose concentration in the reaction mixture is not less than 82%. In a solution with a concentration of 0.04 M, paratoluic acid is almost completely nitrated after only five minutes.

A comparison of the polarogram of a solution obtained after nitration (with subsequent neutralization by KOH) with a polarogram of 3-nitroparatoluic acid shows that 3-nitroparatoluic acid is the acid formed during nitration.

The relationship between diffusion current and paratoluic acid concentration over the concentration range 0.01-4.0 mM/liter, at pH 5.0, is linear.

When terephthalic acid solutions are nitrated under the same conditions a polarographic wave is not obtained.

It is possible therefore to determine paratoluic acid polarographically in the presence of excess terephthalic acid.

Nitroterephthalic Acid. Nitroterephthalic acid was prepared by nitrating terephthalic acid with a mixture of 83% HNO_3 and 8% oleum (1:1) at 60° for 40 min. The product obtained was freed from nitric and sulfuric acid with cold water; it was then dissolved in hot water and the solution filtered on a hot filtration funnel.

The nitroterephthalic acid obtained after being recrystallized twice had a m.p. 272-273° and an acid number 94.7.

In contrast to terephthalic acid, it was not necessary to convert nitroterephthalic acid into a salt in order to dissolve it, since it is itself sufficiently soluble in water.

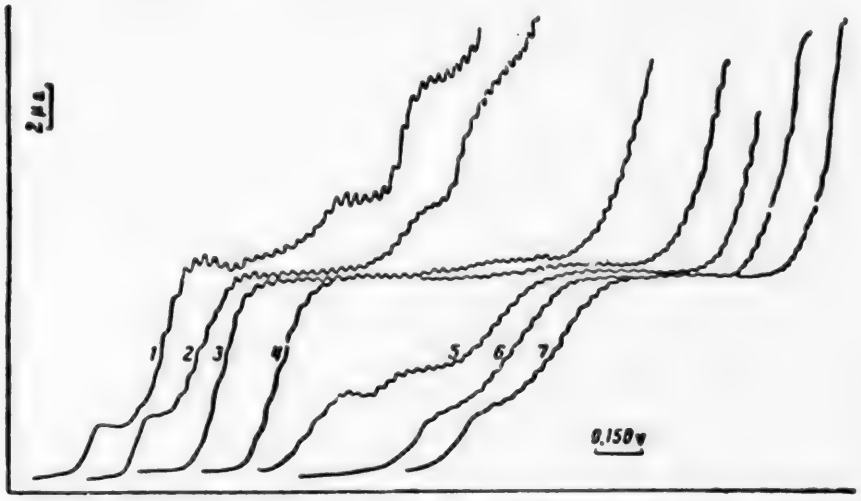

Fig. 3. Polarograms of nitroterephthalic acid at a concentration of 1×10^{-3}M. 1) pH 2.0; 2) pH 4.2; 3) pH 5.0; 4) pH 6.5; 5) pH 8.2; 6) pH 9.2; 7) pH 11.0. Initial voltage 0.04 v.

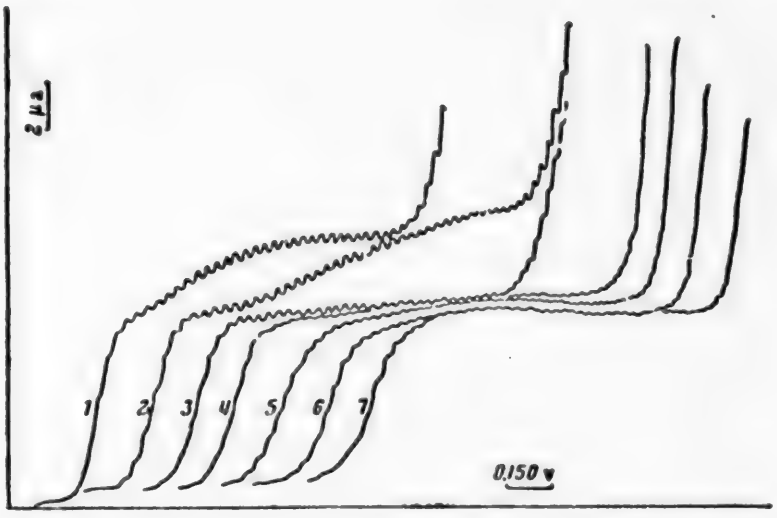

Fig. 4. Polarograms of 3-nitroparatoluic acid at $C = 1 \times 10^{-3}$M. 1) pH 2.2; 2) pH 3.1; 3) pH 4.3; 4) pH 7.4; 5) pH 8.3; 6) pH 9.2; 7) pH 9.7. Initial voltage 0.03 v.

Polarographic waves of nitroterephthalic acid at various pH values of a buffer supporting electrolyte (+0.5 M KCl) are shown in Fig. 3. The nature of the change in the wave with the pH of the supporting electrolyte is similar to that which was observed earlier [5] in the case of nitroterephthalic acids.

It follows from Fig. 3 that the pH range of greatest interest from an analytical point of view is 5.0-6.5, over which one clearly defined polarographic wave is obtained which has a diffusion current constant which is independent of pH, and a half-wave potential $E_{1/2}$ = 0.36-0.45 v which increases with increasing pH.

The relation between i_d and C is linear at pH 6.0; the diffusion current constant I_D = 8.2 ± 0.1 μa/mM/liter (capillary I) over the concentration range 0.01-4.0 mM/liter.

Nitroterephthalic acid can be determined polarographically in the presence of a large excess of terephthalic acid; this is very important for production purposes.

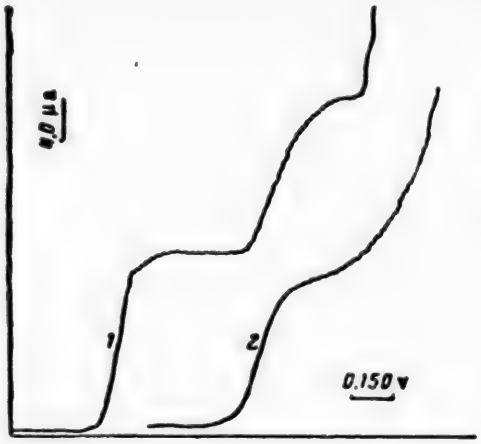

Fig. 5. Polarograms. 1) Dimethyl terephthalate in a supporting electrolyte of 0.05 M $(CH_3)_4$ NI in 80% CH_3OH. Initial voltage 1.2 v; 2) methyl paratoluate in a supporting electrolyte of 0.01 M $(C_2H_5)_4NOH$, 50% CH_3OH. Initial voltage 1.7 v.

3-Nitroparatoluic Acid. The acid was synthesized by nitrating paratoluic acid with 75% HNO_3 at 115° for 6 hours. The suspension obtained, which contained 3-nitroparatoluic acid, was filtered, after cooling, through glass wool and the crystals washed with cold water to free them from nitric acid, the washing process being controlled by means of congo red.

The nitro acid obtained was recrystallized twice from 70% HNO_3.

After purification the product obtained has a m.p. of 189-190° and an acid number of 55.1.

Stock solutions of 3-nitroparatoluic acid were prepared by dissolving the nitro acid in 100% methanol, while polarograms were taken in 20% methanol.

Polarograms of 3-nitroparatoluic acid at various pH values of the buffer supporting electrolyte (+0.5 M KCL) are shown in Fig. 4.

One clearly defined wave whose diffusion current constant is independent of pH is observed at pH 4-8; the half-wave potential $E_{1/2}$ = 0.30-0.65 v, it increases linearly with increasing pH.

The relation between i_d and C is linear. The diffusion current constant is I_D = 7.20 ± 0.04 μa/mM/liter (Capillary I, pH 4.4) over the concentration range 0.01-4.0 mM/liter.

Dimethyl Terephthalate. Commercial dimethyl terephthalate was used (m.p. = 141-142, ester number 103).

Stock solutions were prepared in 100% methanol, while polarograms were taken in 80% CH_3OH in a supporting electrolyte of 0.05 N $(CH_3)_4NI$.

TABLE 1. The Relation between the Limiting Current (i_d) and the Height of the Mercury Reservoir (H)

Test material	Concentration, M	H, cm	i_d, μa	$\frac{i_d}{\sqrt{H}}$, μa·cm$^{-1/2}$
Terephthalic acid	$2\cdot10^{-3}$	33.6	6.48	1.12
		42.0	7.22	1.11
		49.2	7.80	1.11
		58.0	8.62	1.13
Nitroterephthalic acid*	$1\cdot10^{-3}$	34.5	7.50	1.28
		42.0	8.20	1.27
		50.0	9.30	1.30
		58.0	9.90	1.30
3-Nitroparatoluic acid	$5\cdot10^{-4}$	34.5	3.20	0.546
		42.0	3.55	0.547
		50.0	3.90	0.545
		58.0	4.25	0.560
Dimethyl terephthalate*	$2\cdot10^{-3}$	34.5	14.6	2.50
		42.0	16.4	2.56
		50.0	18.0	2.52
		58.0	20.0	2.62
Nitrodimethyl terephthalate*	$1\cdot10^{-3}$	34.5	6.40	1.10
		42.0	6.80	1.05
		50.0	7.20	1.01
		58.0	7.80	1.03

*First wave.

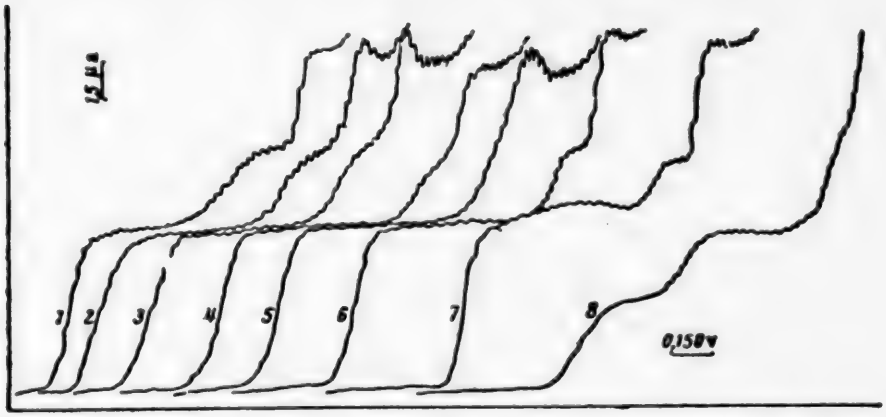

Fig. 6. Polarograms of dimethyl nitroterephthalate at a concentration of 1×10^{-4}M at various pH values of the supporting electrolyte. 1) pH 2.6; 2) pH 3.6; 3) pH 4.7; 4) pH 5.9; 5) pH 6.4; 6) pH 7.8; 7) pH 11.7.

We found that the wave of the ester is not clearly defined enough in acid buffer solutions.

It has been pointed out earlier [2] that the wave height in a supporting electrolyte of $(CH_3)_4NBr$ in 20% dioxane is higher than in a buffer solution. This led us to carry out a detailed investigation of the polarographic behavior of dimethyl terephthalate in methanolic solution in a supporting electrolyte of $(CH_3)_4NI$.

The characteristics of the polarogram of the ester are shown in Fig. 5.

The first wave with $E_{1/2}$ = 1.58 v is of analytical interest. The height of this wave is proportional to the concentration over a very wide range (0.03-6.0 mM/liter). The diffusion current constant I_D = 8.2 ± 0.1 μa/mM/liter (Capillary D).

Methyl Paratoluate. The methyl paratoluate used had a m.p. of 32-35°, and an ester number of 66.0.

Stock solutions were prepared in 100% CH_3OH, while polarograms were taken in 50% CH_3OH; 0.01 N $(C_2H_5)_4NOH$ served as the supporting electrolyte.

The characteristic shape of the polarogram is shown in Fig. 5. The wave obtained has $E_{1/2}$ = 2.12 v. The relation between the diffusion current and concentration is linear.

The diffusion current constant I_D = 2.9 ± 0.1 μa/mM/liter over the concentration range 0.1-8.0 mM/liter (Capillary D.

Dimethyl Nitroterephthalate. The ester used had a m.p. 75-76° and an ester number of 83.4.

Stock solutions of dimethyl nitroterephthalate were prepared by dissolving the nitro ester in 100% CH_3OH, while polarograms were taken in 40% CH_3OH.

Characteristic polarograms obtained at various pH values are shown in Fig. 6.

The one of greatest analytical interest is the first wave obtained at pH 3-7; this wave has a diffusion current constant which is independent of pH and has a half-wave potential $E_{1/2}$ = 0.20-0.45 v.

There is a linear relation between concentration and diffusion current at pH 5.8 (Fig. 7) over the whole concentration range examined 0.02-8.0 mM/liter; the diffusion current constant I_D = 6.1 ± 0.1 μa/mM/liter (Capillary D.

In conclusion we should like to point out that the linear relationship between the limiting current and the square root of the height of the mercury reservoir observed for all the compounds tested (Table 1), indicates that the limiting current has a diffusion character.

SUMMARY

A polarographic study has been made of terephthalic and paratoluic acids, nitroterephthalic and 2-nitroparatoluic

acids, dimethyl terephthalate, dimethyl nitroterephthalate, and methyl paratoluate. With the exception of dimethyl terephthalate this is the first time that these compounds have been studied polarographically.

All the test compounds, with the exception of paratoluic acid, are electrolytically reduced under certain conditions on a dropping mercury electrode to give clearly defined polarographic waves. Paratoluic acid can be rapidly and quantitatively nitrated to give polarographically active 3-nitroparatoluic acid.

The polarographic characteristics of the compounds mentioned above have been examined in aqueous solutions, and, in some case, in water-methanol solutions; it has been established that the limiting current has a diffusion character.

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A RAPID MERCURIMETRIC METHOD FOR THE DETERMINATION OF ISOBUTYLENE IN CRACKING FRACTIONS

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Dobryanskii's sulfuric acid method [1] and modifications of this method [2] can be used for the determination of large amounts of isobutylene. Small amounts of isobutylene are determined by Denige's method [3-5], which is based on the formation of insoluble complexes of tertiary olefines with mercuric sulfate or nitrate. The precipitate which separates out is filtered off, carefully washed until the washings give a negative reaction for Hg^{2+} ions and then dried and weighed or dissolved in concentrated HNO_3 for subsequent thiocyanate titration [6-9]. We shall call the method involving dissolution and thiocyanate titration of the mercury sulfate complex of isobutylene [8] Method A for short, and that involving the mercury nitrate complex [7] Method B. Though these methods are accurate enough they are time-consuming.

The authors of the present article have developed rapid methods (C and D) based on precipitation of isobutylene with a known excess of standard solutions of $HgSO_4$ or $Hg(NO_3)_2$ respectively, dilution of the mixture obtained to a known volume with water or 0.25 N HNO_3, and a thiocyanate titration of aliquots of the supernatant solution. A solution of 33 g $HgSO_4$ in 20% H_2SO_4 [8] is used as the reagent in method C. An aqueous solution of $Hg(NO_3)_2$ with a concentration of 77 g/liter [7] is used as the reagent in Method D.

EXPERIMENTAL

The isobutylene used for preparing synthetic mixtures was obtained by dehydrating trimethylcarbinol in the presence of the sulfopolystyrene cation exchange resin KU-2 in the hydrogen form; β-butylene was prepared by dehydration of secondary butanol with sulfuric acid [9] and was freed from isobutylene which might be present as an impurity with 64% sulfuric acid. On the assumption that the α- and β-isomers behave identically in the test reactions, we shall refer to them in future as n-butylene.

A sample of C_4 hydrocarbon fraction was obtained from the absorption gas fractionation plant of the Novokuibyshevsk Oil Refinery and contained about 12% iso-C_4H_8; 29.8% n-C_4H_8 (total α- and β-butylenes); 13.0% of iso-C_4H_{10}; 39.3% n-C_4H_{10} and small amounts of C_3 and C_5 hydrocarbons present as impurities. The figures quoted were obtained by Dobryanskii's method [1] after low temperature fractionation.

Preliminary experiments, which had as their aim the establishment of the optimum conditions for the formation of precipitates of the complexes of iso-C_4H_8 with mercury salts, were carried out on mixtures of pure isobutylene and air. As a result of these experiments we abandoned the technique recommended in an earlier paper [8] of prolonged formation of the isobutylene complex with mercuric sulfate in the cold, and established that formation of a precipitate is complete in 10 min at 50°.

The isobutylene complex with $Hg(NO_3)_2$ is best formed on heating the test samples with the reagent on a boiling water bath for 15 min. When the isobutylene concentration of test mixtures is not too low, the precipitate with a stoichimetric composition which is formed with the $Hg(NO_3)_2$ solution is not corrected by addition of HNO_3 and NaOH [6]; the pH of such a reagent is 1.55 according to potentiometric titrations.

For the analysis of gas mixtures containing 2-20% isobutylene, 5-50 ml of reagent per 80 ml of test gas is used in method D, while 15 ml of reagent per 20-200 ml of gas is used in method C.

TABLE 1. Determination of Isobutylene by Methods A and C

Mixture No.	No. of determinations	Composition of the mixtures			Iso-C_4H_8 found, vol %		Experimental error (relative), %		Mean deviation of a single determination, %	
		Iso-C_4H_8	n-C_4H_8	Air	Method C	Method A	Method C	Method A	Method C	Method A
1	7	2,00	20,0	78,0	2,15	1,96	+7,5	−2,0	0,08	0,09
2	4	4,00	10,0	86,0	4,15	3,99	+3,8	0,0	0,08	0,12
3	7	9,80	27,5	62,7	10,2	10,0	+4,1	+2,0	0,12	0,13
4	4	12,50	12,5	75,0	12,3	12,3	−1,6	−1,6	0,12	0,16
5	4	19,20	9,6	71,2	19,7	19,6	+2,6	+2,5	0,27	0,27

TABLE 2. Determination of Isobutylene in Synthetic Mixtures by Methods B and D

Mixture No.	No. of analyses	Composition of the mixtures, vol %			Iso-C_4H_8 found, vol %		Experimental error (relative), %		Mean deviation of the measurements, %	
		Iso-C_4H_8	n-C_4H_8	Air	Method D	Method B	Method D	Method B	Method D	Method B
1	11	2,00	20,0	78,0	1,65	1,56	−17,5	−22,0	0,15	0,18
2	6	4,00	10,0	86,0	4,33	4,35	+ 8,3	+ 8,7	0,12	0,17
3	4	9,80	27,5	62,7	10,5	10,3	+ 7,2	+ 5,1	0,29	0,34
4	8	12,50	12,5	75,0	13,2	12,8	+ 5,6	+ 2,4	0,13	0,11
5	5	19,20	9,6	71,2	20,4	20,6	+ 6,2	+ 7,3	0,30	0,21

Determination of isobutylene by means of the mercuric salts reduces to the following operations.

a) Determination of Isobutylene by Method C. A known volume of test gas supplied from a gas buret is passed for 15-20 min through a capillary into a test tube 20 cm long and 10 mm in diameter filled with a known volume of reagent. The test tube is then placed for 10 min in a water bath at a temperature of 50°. After the time indicated above has elapsed, liquid plus precipitate are quantitatively transferred to a 100 ml standard flask; water is used for washing the capillary and test tube. The contents of the standard flask are made up to the mark with water, and after the flask has been allowed to stand for one hour, a 20-25 ml aliquot is taken and treated with a saturated solution of $KMnO_4$ until a permanent rose color is obtained. Excess oxidizing agent is reduced with 2% H_2O_2, after which the solution is titrated with 0.1 N NH_4SCN.

b) Determination of Isobutylene by Method D. A known volume of mercuric nitrate is introduced into a 250 ml round-bottom flask. The flask is stoppered with a cork fitted with a three-way tap and is evacuated for 2-3 min using a prevacuum pump.

A known volume of gas is introduced from a gas buret into the evacuated flask, the flask is vigorously shaken for 5 min, it is then opened to the atmosphere and shaken again for a further 2 min; it is finally placed on a boiling water bath for 15 min. The mixture obtained is cooled, quantitatively transferred to a 250 ml standard flask, and its volume made up to the mark with 0.25 N nitric acid.

Twenty five ml of the supernatant liquid is taken, 1 ml of concentrated sulfuric acid, and 0.5 ml of a saturated solution of ferric ammonium alum are added, followed by a saturated $KMnO_4$ solution, until a bright-rose color is obtained. Excess permanganate is destroyed by addition of 2% hydrogen peroxide and the solution titrated with 0.1 N NH_4SCN.

Calculations of the isobutylene content of the gas mixtures were made on the assumption that one millimole of olefine in the complex with $Hg(NO_3)_2$ and $HgSO_4$ is equivalent to 6 mg-ion of Hg^{2+}. These relationships correspond to the following probable formulas of the precipitates:

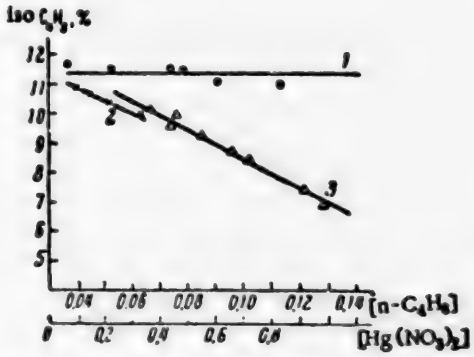
$$[HgNO_3 \cdot Hg(NO_3)_2]_2 \cdot C_4H_8 \text{ [10]; } \left[O\begin{matrix}Hg\\ \diagup\\ \diagdown\\ Hg\end{matrix}SO_4\right]_2 \cdot C_4H_8 \text{ [8].}$$

TABLE 3. Determination of Isobutylene in Production Fractions

Isobutylene content in the test sample, %	Isobutylene found (in %) by methods:			
	C	D	B	A
12.1	11.8	11.6	11.3	10.4
6.0	5.9	5.6	5.6	5.4
1.2	0.96	0.96	0.96	0.93

A comparative evaluation of methods A, B, C, and D can be made on the basis of the results of the determination of isobutylene in synthetic mixtures containing air and n-butylene (Tables 1 and 2). Each result is the arithmetic mean of 4-11 determinations.

The results given in Table 1 illustrate that satisfactory agreement is obtained between the results for determination of isobutylene by means of methods A and C. The experimental error of method C increases with increasing relative content of n-butylene, which (though slowly) is also capable of reacting with $HgSO_4$ to form a sparingly soluble complex [8].



The effect of the value of the molar ratio n-C_4H_8: $Hg(NO_3)_2$ on the results of determining isobutylene in synthetic gas mixtures. 1) Mixture of 11.3% iso-C_4H_8, 10% n-C_4H_8, and 78.7% air (upper scale); 2) mixture of 10.5% iso-C_4H_8, 27.5% n-C_4H_8, and 62.0% air (lower scale); 3) mixture of 10% iso-C_4H_8 and 90% n-C_4H_8 (lower scale).

It can be assumed that small amounts of this complex are coprecipitated with the corresponding derivatives of isobutylene, thereby increasing the amount of reagent used up in the reaction. Subsequent washing of the precipitate, presumably leads to partial dissolution of the complex of n-butylene with $HgSO_4$, and to a slight increase in the accuracy of the determination of isobutylene.

The reproducibility of the experimental results, which is characterized by the value of the mean deviation of one measurement, is almost the same in both methods.

The results given in Table 2 lead one to doubt Isakova and Rakhmanina's opinion [7] that mercuric nitrate is preferable to mercuric sulfate. Actually, on using a solution of $Hg(NO_3)_2$ as reagent, methods B and D give results which are less accurate and have a poorer reproducibility than methods A and C.

If it is assumed that buylenes with normal structure do not react with $Hg(NO_3)_2$ [6, 7], then the positive experimental errors can be related to occlusion of some of the reagent by the precipitate formed.

This treatment cannot, however, be extended to cover the analysis of mixture No. 1 with a low isobutylene content (2.00%) and a large excess of n-butylene, for which considerable negative errors are obtained.

The important question therefore arises: is it not possible to assume simultaneous formation of a soluble mercuric complex with n-butylene which complexes Hg^{2+} ions and displaces the equilibrium of the precipitation reaction $[HgNO_3 \cdot Hg(NO_3)_2]_3 \cdot$ iso-C_4H_8 so that the precipitate dissolves? Such an assumption is confirmed by the results of a study of the relationship between the isobutylene content of different gas mixtures based on analytical results and the number of millimoles of n-butylene which are equivalent to 1 millimole of unreacted $Hg(NO_3)_2$ (diagram).

Curve 1, constructed on the basis of the analysis of mixtures with an almost equal content of isobutylene and n-butylene, exhibits the usual statistical scatter of experimental points determined by the reproducibility of the experiments.

Curves 2 and 3 show a definite trend in the experimental points, which indicates an increase in negative experimental errors with increasing relative n-butylene content (from 10 to 90 vol. %) and with increases in the ratio of the number of millimoles of n-butylene in a test sample to the number of millimoles of $Hg(NO_3)_2$ which do not react with isobutylene.

At low molar ratios of $[n\text{-}C_4H_8] / [Hg(NO_3)_2]$ (corresponding to a small volume of test mixture or to a considerable amount of reagent) complete precipitation of isobutylene occurs, with occlusion of reagent leading to positive experimental errors.

At high molar ratios of $[n\text{-}C_4H_8]/[Hg(NO_3)_2]$ formation of a soluble complex of n-butylene with $Hg(NO_3)_2$ with simultaneous dissolution of the precipitate $[Hg\ NO_3 \cdot Hg(NO_3)_2]_3 \cdot C_4H_8$ is probable. These phenomena lead to incomplete precipitation of isobutylene, and, consequently, to negative experimental errors.

In order to prove formation of soluble complexes, the partition coefficients of Hg^{2+} ions between KU-2 resin in the H-form and a $Hg(NO_3)_2$ solution in the presence and in the absence of n-butylene were determined. K_D values calculated on the basis of the analytical results of equilibrium solutions [11] as the ratio of the number of meq Hg^{2+} calculated on one g of resin, to the number of meq Hg^{2+} in 1 ml of solution, were 5.80 and 9.84 respectively.

The decrease in the value of K_D in the presence of n-butylene is a direct indication of the formation of soluble complexes with $Hg(NO_3)_2$.

Similar phenomena are also possible during the interaction of n-butylene with $HgSO_4$. In the case of the analysis of small volumes of mixtures of 10% isobutylene and 90% n-butylene, coprecipitation of an insoluble complex of iso-C_4H_8 with the insoluble complex of n-C_4H_8 occurs, which leads to a positive experimental error. When a large volume of this gas mixture is analyzed (the same amount of reagent being used), the n-butylene present in excess can complex the mercury ions to form a soluble complex (which is titrated by the ammonium thiocyanate), which leads to dissolution of part of the precipitated complex of isobutylene with $HgSO_4$ and is responsible for the negative experimental error.

In future it will be necessary to undertake a systematic study of the conditions leading to the formation of, and the composition of the complexes of iso- and n-butylene with mercury salts and to correct the conversion factors included in the latest monographs [9, 10].

Until such work is carried out the methods which we have suggested can be used for determining isobutylene in mixtures which do not contain too high a percentage of n-butylene.

In order to check on the applicability of methods C and D to the analysis of industrial hydrocarbon mixtures, the isobutylene content of fractions from the absorption gas fractionation unit of the Novokuibyshevsk Oil Refinery was determined. Results of the analyses of the original fractions and of the same fractions after being diluted with air, by means of methods A, B, C, and D are compared in Table 3.

As the results in Table 3 show, the methods compared give results which are in agreement with each other. The time taken to carry out methods C and D is about a third of that required for methods A and B.

SUMMARY

A new, rapid method is suggested for the determination of isobutylene in its mixtures with n-butylenes; it is based on precipitation of the hydrocarbon to be determined with a known excess of a standard mercuric sulfate of nitrate solution, dilution of the mixture obtained to a known volume with water or 0.25 N HNO_3, and titration of an aliquot of the supernatant liquid with standard NH_4SCN solution. Precipitation of the complex of isobutylene with mercuric sulfate gives more accurate and reproducible results than those obtained when mercuric nitrate is used as precipitant.

The analytical methods developed have been used for determining the isobutylene in C_4 hydrocarbon fractions from the gas fractionation unit of the Novokuibyshevsk Oil Refinery.

Some suggestions are advanced re complex formation between n-butylene and mercuric sulfate and nitrate.

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BRIEF COMMUNICATIONS

INCREASING THE SENSITIVITY OF DETERMINATION BY MEANS OF A DISCHARGE IN A HOLLOW CATHODE

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The sensitivity of the determination of many elements is very high when high temperature discharge conditions in a hollow cathode [1-3] are used as a light source. An attempt is made in this note to evaluate the limiting absolute sensitivity of the determination of various elements. The work was carried out on the setup described previously [1, 2]. The helium pressure in the discharge tube was 15 mm Hg, and the discharge current was 1100 ma. The design and dimensions of the graphite cathodes are shown in the diagram. A layer of polystyrene was deposited on the face of the capsule by evaporating a drop of a dichloroethane solution of polystyrene; a solution of the test element was then placed in the same position. After this solution had been evaporated, an outer cylinder was fitted onto the capsule and the cathode placed in the discharge tube. Requisite precautions for preventing accidental contamination were taken during all the operations. The results obtained, expressed in mμg (10^{-9}g), and also the corresponding results for the "copper spark" method and the fractional distillation method involving the use of a carrier [4] are given in the table. The analytical lines used are also included in the table. It should be borne in mind that the results relating to the last two methods were obtained by means of a Baird diffraction spectrograph, which has a considerably higher dispersion than the ISP-22 and ISP-51 spectrographs fitted with a UF-84 camera (the latter for determing sodium, lithium, and potassium) which we used. It can be assumed that the sensitivity with which lithium and elements whose analytical lines are located in the 2800-5000 A region can be increased (to differing extents for different elements) by using apparatus with a higher dispersion, and correspondingly more sensitive photographic materials.

The results given for a hollow cathode correspond to an increase of the blackening of the analytical line over the background of 0.05-0.10. Thus the sensitivity criterion for all the results included in the table is approximately the same. As these results show, the sensitivity of a determination by means of a discharge in a hollow cathode is in many cases considerably higher than in the most sensitive of the direct methods of spectrographic analysis. This fact can be used for increasing the sensitivity of analyzing pure solutions. The use of a discharge tube with a hollow cathode during the analysis of concentrates of impurities in chemicospectographic methods of analysis permits the sensitivity to be increased essentially in these cases also. The list of elements which can be determined in this way can be considerably extended.

In principle, the technique described should permit determination of all elements whose volatility (more accurately, the volatility of their appropriate compounds) under the specific conditions of a high temperature discharge in a hollow graphite cathode is close to the volatility of the elements included in the table. On the basis of the results obtained here one should be able to get an approximate idea of the sensitivity of determination which is attainable in these cases. The method suggested is, however, not suitable for the determination of many elements which form stable compounds with low volatility under the conditions described. In particular, the sensitivity of the determination of thorium, uranium, tantalum, niobium, tungsten, zirconium, and molybdenum proved to be very low. Photographs of the spectra of spark discharges using capsules as electrodes, showed that on treating the capsules in a discharge in a hollow cathode, the elements indicated remain almost completely on the surface of the capsules.

Element	Analytical line (A)	Sensitivity, mμg (10^{-9} g)		
		Hollow cathode*	"Copper spark"**	Fractional distillation with a carrier**
Al	1 3092,7	10+	10	500
Ag	1 3280,7	0,03	—	5
B	1 2497,7	1	10	1
Be	11 3130,4	0.03	0,2	10
Cd	1 2288,0	30	200	7
Co	1 3453,5	0,3	50	100
Cr	11 2835,6	1	5	300
Cu	1 3247,5	0,03	—	30
Fe	11 2599,4	3	50	100
Ga	1 2943 6	0,03	100	—
K	1 7664,9	10	10	200
Li	1 6707,8	0,1	0,2	10
Mg	1 2852,1	0,03'(~0,0001)	1+(0,1)	50
Mn	1 2794,8	0,03	2	100
Na	1 5889,9	0,03	10+	50
Ni	1 3050,8	1	10	200
P	1 2535,6	30	2000	5000
Pb	1 2833,1	10	5	100
Sb	1 2528,5	100	500	1000
Si	1 2881,6	1	10	300
Sn	1 2840,0	10	—	100
Zn	1 3345,0	3	200	2000

*Absolute sensitivity when pure solutions were used.

**Absolute sensitivity obtained by conversion from the concentration sensitivity for the main elements having a complex spectrum (100 mg U_3O_8 + Limit determined by impurities. The figures in brackets are limits which can be attained in the absence of impurites.

An interesting feature is that the sensitivity with which some elements (beryllium, silver, copper, manganese, gallium, sodium, and particularly magnesium) can be determined is fairly close to the theoretical limiting sensitivity for a discharge in a hollow cathode (10^{-13} g), calculated very roughly by Mandel'shtam and Nedler [5].

SUMMARY

The absolute values of the sensitivity of the determination of a number of elements using high temperature discharge conditions in a hollow graphite cathode have been established. The sensitivity with which most elements can be determined, with the exception of the least volatile ones, is considerably higher than the sensitivity which is possible when the same elements are determined by fractional distillation in a dc arc using a carrier, and by the "copper spark" method.

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NORMAL AND LOGNORMAL DISTRIBUTION OF RANDOM ERRORS IN QUANTITATIVE SPECTROGRAPHIC ANALYSIS

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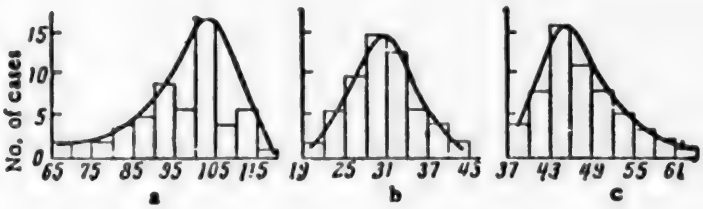
It is pointed out in textbooks on spectrographic methods of analysis that the distribution of random errors during the determination of the content of an element conforms to Gauss' normal law. This is in accordance with the well-known rule that the direct results of a physical experiment or measurement are subjected to the normally distributed random error. Ahrens [1], however, has generalized all the information on the asymmetric distribution of the errors in spectrographic determination, and has pointed out that this distribution is best described by the so-called lognormal law. This means that the asymmetric (with a taper on the right) distribution of the concentrations found becomes normal after a logarithmic transformation. In this case, treatment of the results by the methods of ordinary mathematical statistics is approximate, and, as Ahrens has shown, unsatisfactory, when the error is greater than ± 15%.

We have carried out several series of determinations of various elements in a series of samples – about 60 parallel determinations in each series. Curves constructed on the basis of the results of one series are shown in the diagram. The results of the other series are similar. In all cases the distribution of the concentrations measured (i.e. the distribution of the experimental error) approximates to a lognormal distribution (fig. c).



Distribution curves of the results of a spectrographic analysis. a) Antilognormal distribution of the blackening S; b) normal distribution of ΔS and log C; c) lognormal distribution of the concentration C.

The contradiction which arises can be eliminated, in our opinion, as follows.

As is known, the value of the concentration is found by means of the following formula:

$$\frac{S_1 - S_2}{\gamma b} = \lg C_1 - \lg C_2.$$

Here S_1 is the blackening of the analytical line, S_2 is the blackening of the line of the internal standard or background, γ is the contrast factor of the photographic plate (approximately 1), b is the selfabsorption coefficient of the line which is usually equal to one in the working region, C_1 is the concentration being determined, and C_2 is the concentration of the internal standard.

The blackening values S_1 and S_2 are measured directly and $\Delta S = S_1 - S_2$ is calculated. It is assumed that $\log C_2 = \text{const}$, and a linear relationship is established between ΔS and $\log C_1$ (with a slope of γb).

In our experiments we studied the types of distribution curves for all the factors which enter into the formula indicated. We established that the distribution of S_1 and S_2 is antilognormal* (Fig. a), i.e., it is asymmetric, tapering to the left.

The distribution of S_1 and S_2 should correspond to the distribution of log C_1 and log C_2 (the correspondence being better the nearer γb is to 1). The distribution of the logarithms of the concentrations of the test element and the internal standard should also be antilognormal, and, consequently, the distribution of the concentration (i.e., the experimental error) should be normal, in complete accord with the assumptions of most spectroscopists.

Thus the distribution of log C_1 corresponds to the distribution of S_1, but not ΔS. ΔS – the difference between the two asymmetric distributions S_1 and S_2 – is an almost normal distribution** (Fig. b). It follows from this that when, using a linear curve (working), values of log C_1 are sought, which correspond, according to the basic formula, to ΔS values, one will inevitably obtain for log C_1 a distribution approximating to a normal rather than an antilognormal distribution for C_1 (since the logarithms of the concentration are distributed normally, Fig. b).

During treatment of several parallel results for one sample, one usually calculates the mean arithmetic value and the mean arithmetic or mean square error.

Nevertheless, a mathematical study of a lognormal distribution [2] shows that it is characterized by three different values – the mean arithmetic am, the mean geometric gm, and the most probable value y_{max}, between which the following relationships hold:

$$\lg am = \lg y_{max} + 3{,}4539\lambda^2,$$
$$\lg am = \lg gm + 1{,}1513\lambda^2,$$

where λ is the mean square deviation of the logarithms of the values (distributed normally) from their mean arithmetic value. The latter corresponds to the mean geometric value of the lognormal distribution considered, not to its mean arithmetic value.

This means that the mean arithmetic value of ΔS corresponds not to the mean arithmetic value of C, but to their geometric value.

It can be shown that for an experimental error of, e.g., ± 5%, the mean arithmetic value will only exceed the mean geometrical value by about 0.1%, for an error of ±10% by about 0.5%, for an error of ±20% by 2%, and for an error of ±25% by 3%.

Thus the statistical error in the treatment of results has an essential effect only at high reproducibility errors (>10-15%).

A simple method can be suggested, however, whereby the error arising during calculation can be completely eliminated.

It must be borne in mind that as a result of the linear relation between ΔS and log C, the value of ΔS_{mean} corresponds accurately to log C_{mean}. This means that the correct value of C_{mean} corresponds to the antilogarithm of log C_{mean} and is the mean geometrical value for the lognormal distribution of C. This correct value of C is found more simply by calculating ΔS_{mean} and log C_{mean}. The experimental error can also be accurately calculated by means of the normally distributed values of ΔS or log C***.

For conversion from errors in the values of ΔS_{mean} or log C_{mean} to errors in the value of C_{mean} the following formula [3] can be used:

$$\varepsilon/C\% = 2{,}3\lambda \cdot 100,$$

*The distribution of S is called antilognormal because the values of S from the formula $S = -\log a + 3 = \log 1/a + 3$ correspond to the antilogarithm of the values of 1/a (a is the transmissivity), the distribution of which, as established in the same experiments, is normal.

**Under these conditions the distribution of ΔS will become closer to a normal distribution, the nearer is the distribution of S_2 to the distribution of S_1, i.e., the better the choice of internal standard or the better the continuous background "works" with the analytical line.

***The characteristics calculated for ΔS will be closer to the true value, the less the slope of the curve differs from 45° (i.e., γb from 1). Accordingly, it is more accurate to use the values of log C.

where $\epsilon_{C\%}$ is the relative error for C_{mean}, and λ is the mean square error for ΔS_{mean} or $\log C_{mean}$.

SUMMARY

The reason for the lognormal distribution of random errors during determination of the concentration of an element is discussed. It is shown that this phenomenon does not correpond to the physical nature of the spectrographic method, but is the result of the way in which spectrographic analysis data is treated. A method of eliminating the statistical error is suggested.

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DOUBLING OF THE MASS SPECTRUM OF CESIUM

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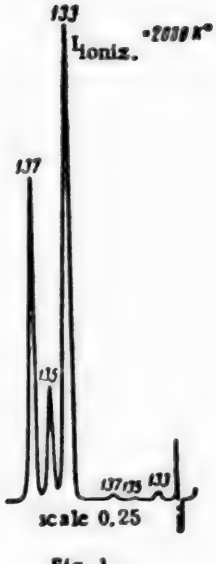

Fig. 1

The technique most often used at present for obtaining ions during mass-spectrometric analysis of solids is ionization on an incandescent surface. During the analysis of elements with low ionization potentials an ion source of this type is very efficient. The work was carried out with a ribbon type ion source which is part of the MS-4 mass-spectrometer. During the analysis of cesium isolated from the fission products of uranium 235, we observed doubling of the mass-spectrum of cesium; in addition to the main mass spectrum, a satellite spectrum (Fig. 1) appeared at a certain temperature of the ribbon source. This effect was observed when the temperature was increased considerably and when the ion source had been used for a long time with the test element. As the temperature increased the intensity of the peaks in the general mass-spectrum of cesium increased sharply (Fig. 2). The isotopic composition of cesium, calculated on the basis of the fundamental spectrum and on the basis of the satellite spectrum remained the same. We think that the mechanism of this phenomenon is as follows. The neutral cesium atoms evaporating from the ribbon when the source is operating condense on the colder parts of the source, including the edges of the lens slit standing close to the screen. During prolonged operation the edges of the slits of these lenses are strongly heated and when the temperature reaches about 500°, ionization of the cesium ions on this surface is possible. The ions formed will have an energy differing from the energy of the ions formed on the ribbon itself by the value of the stretching voltage. They will be recorded as ions of lower mass. This explanation of the doubling effect can be confirmed by calculation.

The possibility of the appearance of additional peaks in the general mass spectrum, as the result of the formation of ions with a different energy, must be taken into account during the mass-spectrometric analysis of readily ionizable elements.

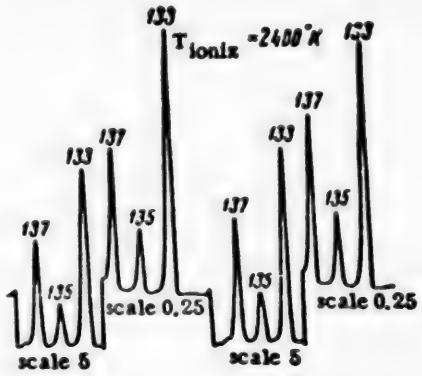

Fig. 2

SUMMARY

Doubling of the mass spectrum of cesium has been observed during the mass-spectrometric analysis of cesium isolated from the fission products of U 235.

It has been shown that this is the result of the ionization of cesium ions along the edges of the slit of the stretching lens.

DETERMINATION OF THE ISOTOPIC COMPOSITION OF OXYGEN IN SOLIDS

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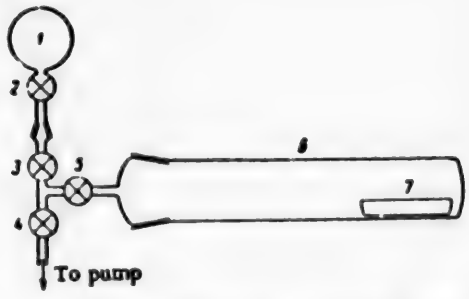
During studies of the isotopic exchange of oxygen in systems which include solids, the reaction kinetics in most cases are determined by the change in the isotopic compostion of the gas or liquid phase. Thermal or chemical decomposition methods, and also exchange with water are used for determining the isotopic compostion of solids. For mass-spectrometric measurements, the oxygen is usually converted into CO_2 (O_2 is used less frequently). In the case of thermostable materials or materials which exchange with difficulty however, these methods are not suitable. In addition, at low degrees of exchange, and when oxygen enriched to only a small extent with the heavy isotope is used, the error in determining the O^{18} content, as a result of dilution and side exchange reactions, is of the same order as the exchange effect it is desired to determine. When carbon is used as a reducing agent it must be borne in mind that at a reducing temperature in excess of 800° expensive apparatus is required, since in such cases quartz exchanges with CO_2 and O_2 at an appreciable rate.

Comparison of the Isotopic Composition of Oxygen in Some Solids as Determined by Gas Exchange and by their Reduction with $K_4[FE(CN)_6]$

Composition of the solid phase	Isotopic composition (in at.%) as determined by:	
	Gas exchange	Reduction of the solid phase
Al_2O_3	0,470	0,471
Li_2SO_4	0,328	0,332
$BaSO_4$	1,560	1,544
$Ba_3(PO_4)_2$	0,260	0,263
Na_2WO_4	0,250	0,254

Potassium ferrocyanide $K_4[Fe(CN)_6]\cdot 3H_2O$ has proved to be a very convenient reducing agent. By heating in a drying oven to 100° for a short time it is possible to prepare the very pure anhydrous salt, which, on heating above 400°, decomposes readily. The melt obtained, which contains finely divided carbon, is capable of reducing a wide variety of materials at a temperature of about 600°. The absence of oxygen in the reducing agent, and the low reducing temperature, eliminate the necessity of applying corrections to the directly measured isotopic composition of the oxygen in the CO_2 obtained. It is also possible to use quartz for making the requisite apparatus.

The apparatus used for preparing CO_2 samples during isotopic analysis of oxygen in solids of the oxide and salt type is shown in the diagram; it is simple to make and to operate. An aliquot of test salt or oxide (about 20 mg) is mixed with an equal volume of $K_4[Fe(CN)_6]$



Apparatus for preparing CO_2 samples during the isotopic analysis of oxygen in solids. 1) Receiver for CO_2 samples; 2-5) taps; 6) quartz test tube with a ground joint; 7) boat with aliquot of test material and $K_4[Fe(CN)_6]$.

and placed in a porcelain boat in a quartz test tube 6, whose volume should not be less than 30 ml. While the tube is heated with a gas burner to 150-200° the mixture is trained (aged) in a vacuum at 10^{-3}-10^{-4} mm Hg in order to remove traces of water and adsorbed air. The aging period is 10-30 min, and depends on the state of the preparation. Tap 5 is then switched over, the temperature is taken up to 600° and after 3-5 min with tap 4 closed the mixture of CO_2 and N_2 formed is transferred into receiver 1 provided with a standard ground joint which enables it to be connected to a mass-spectrometer. The accuracy with which the isotopic composition of oxygen can be determined depends on the quality of the mass-spectrometer. When solids are used in which the isotopic composition of the oxygen is not uniform with the depth of the crystals, the amount of $K_4[Fe(CN)_6]$ in the mixture must be increased, and complete reduction of the test material is achieved by increasing the heating time during decomposition.

The author has used this method for the analysis of the isotopic composition of oxygen in Al_2O_3, Na_2SO_4, $BaSO_4$, $Ba_3(PO_4)_2$, Na_2WO_4, Na_2MoO_4, and obtained very good results (see table).

SUMMARY

Most oxygen-containing solids can be reduced with $K_4[Fe(CN)_6]$ at temperatures below 600° in a simple quartz apparatus. The isotopic composition of CO_2 obtained agrees accurately with the isotopic composition of test materials obtained on complete reduction. The amount of test material required for analysis is 10-20 mg.

A RAPID METHOD FOR DETERMINING COPPER IN CADMIUM METAL AND CADMIUM SALTS BY MEANS OF POTASSIUM FERROCYANIDE

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Methods used for the determination of copper in cadmium metal and cadmium salts include the dithizone extraction titration method [1], and photometric diethyldithiocarbamate method [2], and spectrographic methods [3]. Current standards, however, do not set a limit on the permissible amount of copper in many cadmium salts ($CdCl_2$, $Cd(NO_3)_2$, $Cd(CH_3COO)_2$ and $CdCO_3$) and only a qualitative test is given for copper, in which ammonia is used [4-7]. Since the methods mentioned above take a long time and cannot always be carried out in plant laboratories (e.g., the spectrographic method), while the ammonia method, in view of its low selectivity, should be replaced in the GOST methods by a better method, we thought that it would be expedient to describe in this communication a new, very simple, and rapid method for determining copper in cadmium and its salts.

The method is based on coprecipitation of traces of copper on cadmium ferrocyanide as collector [8], followed by a comparison of the intensity of the rose color of the precipitate with the colors of standard series of precipitates prepared under the same conditions, using the respective pure salts of cadmium to which copper has been added in the form of a standard solution.

Samples tested	Copper found, %	
	By the suggested method	By the dithizone method
Granulated cadmium metal ("analytical grade")	0.004	0.0045
Cadmium rods (K_DO grade)	0.003	0.0035
Cadmium metal (standard sample No. 177)	0.007	0.006
Cadmium chloride ("analytical grade")	0.0004	0.0005
Cadmium bromide ("analytical grade")	0.0004	0.0005
Cadmium iodide ("analytical grade")	0.0003	0.0004
Cadmium nitrate ("analytical grade")	0.0004	0.0003
Cadmium carbonate ("analytical grade")	0.0004	0.0004
Cadmium sulfate ("analytical grade")	0.0002	0.0003

On adding the first drops of K_4 [$Fe(CN)_6$] solution to a solution containing up to 100 mg Cd^{2+}, and up to 10 mg Cu^{2+}, up to 80% of the copper will be found in the $Cd_2Fe(CN)_6$ precipitate formed; as a result the precipitate is colored a weak rose-color (a precipitate of pure $Cd_2Fe(CN)_6$ is white in color). As the copper concentration in the original solution increases (when a constant amount of precipitant is used) the color intensity of the precipitate also increases. Coprecipitation of copper is greatest when the concentration of the cadmium salt is 1% and when a 0.5-1.0% $K_4Fe(CN)_6$ solution is used.

By varying the amount of solution and taking the minimum amount of precipitant, it is possible to determine down to 2×10^{-4}% copper; this means that it is possible to ensure control of the purest commercial cadmium salt available – chemically pure grade cadmium sulfate [2].

Analytical Procedure. 0.5 g of cadmium metal mark K_DO (or 0.25 g of mark K_D1 and K_D2) is dissolved on heating in a few ml of HNO_3 and the solution evaporated to dryness on a sand bath. The residue is transferred to a 100 ml standard flask and is made up to the mark with water. Twenty ml of the solution obtained is placed in a 25 ml cylindrical centrifuge tube with a spherical bottom and 0.5 ml of freshly prepared $K_4Fe(CN)_6$ solution added dropwise with continuous stirring. The liquid is allowed to stand for 10 min in order to allow the colloidal solution formed initially to coagulate, after which the precipitate is centrifuged for one minute at 1000 rpm. The solution is poured as completely free as possible from the precipitate, 2-3 drops of water are added and the precipitate stirred up until a homogeneous suspension is obtained. The precipitate is allowed to stand for 3-5 min, after which its color is compared with the colors of a standard series of precipitates prepared under the same conditions from samples of cadmium metal with a known copper content, or using reagent grade $Cd(NO_3)_2$ free from copper but to which known amounts of copper are added.

This method permits determination of down to 0.001% copper to cadmium metal. One determination takes 30 min.

If results are not required in the shortest possible time, the centrifuging stage can be omitted, and the precipitate simply allowed to settle. In such cases it is recommended that 60-110 ml tall cylindrical test tubes with spherical bottoms be used; 50-100 ml of solution containing 0.25-0.50 g of cadmium (mark K_DO or "analytical grade" material) is introduced into such test tubes, and from 0.5 to 2.0 ml of 0.5% $K_4Fe(CN)_6$ added. The test tube is stoppered with a cork, its contents carefully mixed and then allowed to stand for 3-4 hours. At the end of this period, without pouring off the solution above the precipitate, the test tube is rapidly rotated by hand, the tube being held in a vertical position and shaking avoided. During this operation the precipitate collects in the lower part of the test tube into a compact mass, and its color is compared in this form with the color of a standard series of precipitates prepared in a similar way. For convenience of observation it is recommended that a narrow movable mirror surface be fixed in the lower strip of a support. By lifting the test tube slightly and fixing the mirror at an angle to the observer, it is possible to examine the color of the precipitates easily.

Determination of down to 0.0002% copper in cadmium salts is carried out as follows.

One g of salt (weighed to an accuracy of 0.01 g) is dissolved in 100 ml of distilled water in a 150 ml beaker. From 5 to 10 drops (accurately) of 0.5% $K_4Fe(CN)_6$ is added with continuous stirring. The mixture is transferred as rapidly as possible into two 50 ml centrifuge tubes in which it is centrifuged for 5 min at 1500-2000 rpm. The solution is poured off almost completely from the precipitate, about 0.5-1.0 ml of centrifugate being left behind; the precipitate adhering to the bottom is stirred up to give a suspension in this volume. The suspension from both tubes is trans-

ferred into a 3-4 ml conical centrifuge tube and again centrifuged for one minute at 1000 rpm. The color of the precipitate, which has a volume of 20-30 mm³, is compared with the color of a standard sample prepared at the same time as the test material and under the same conditions from the appropriate cadmium salt, containing a known amount (permitted by GOST specifications) of copper. For this purpose it is expedient to use a large diameter lens with a magnification of 2-3.

A determination takes 10-15 min.

A standard copper solution is prepared by dissolving electrolytic copper in HNO_3 (1:1); the solution is evaporated with H_2SO_4 to the appearance of white fumes, and the solution is finally transferred to a standard flask.

A stock solution of $K_4Fe(CN)_6$ is prepared by dissolving 50 g of its crystallohydrate in one liter of water. The solution will keep unchanged for several months in a dark vessel. 0.5% solution is prepared by appropriate dilution of the stock solution. The dilute solution will keep for 5-7 days.

The method developed for the determination of copper by means of $K_4Fe(CN)_6$ gives satisfactory results (see table) and can be recommended as a rapid method in technical analysis for controlling the production of cadmium metal and salts.

SUMMARY

A rapid method has been developed for the determination of copper in cadmium metal and cadmium salts. The method consists of the following: 0.5-1.0 ml of 0.5% $K_4Fe(CN)_6$ solution is added to a 1% solution of cadmium salt; the precipitate is centrifuged and the intensity of its rose color compared with the colors of a standard series of precipitates which are prepared under identical conditions.

The sensitivity of the method is for cadmium metal 0.001% of Cu and for cadmium salts 0.0002% of Cu.

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THE USE OF MAGNESIUM FERROCYANIDE FOR THE TITRIMETRIC DETERMINATION OF POTASSIUM IN PLANT MATERIALS

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We recommend $Mg_2[Fe(CN)_6]$, which is superior to $Ca_2[Fe(CN)_6]$ used earlier [1], for the determination of potassium. SO_4^{2-} and small amounts of PO_4^{3-} ions do not interfere with determination of potassium by means of $Mg_2[Fe(CN)_6]$. It is prepared by adding an excess of an aqueous suspension of magnesium oxide to a washed precipitate of $H_4[Fe(CN)_6]$ obtained by adding concentrated HCl to a saturated solution of $K_4[Fe(CN)_6]$.

On adding ethanol to the aqueous solution containing potassium ions and excess magnesium ferrocyanide, the precipitate separates out rapidly and its composition corresponds accurately to the formula $K_2Mg[Fe(CN)_6]$.

Nevertheless, magnesium ions form precipitates of varying composition with potassium ferrocyanide under different precipitation conditions; thus when a solution of potassium ferrocyanide is added to an aqueous ethanol solution of a magnesium salt in the presence of excess potassium chloride, a precipitate of the composition $MgK_{12}[Fe(CN)_6]$ is formed [2].

The minimum ethanol concentration established empirically is 32% by volume. At higher ethanol concentrations, and when different precipitation conditions are used, the precipitate forms slowly [3]. At ethanol concentrations of about 50% the reagent itself starts to precipitate out, even in the absence of potassium ions; determinations are then impossible. It has been shown that potassium can be determined in the form of $5Cd_2[Fe(CN)_6] \cdot 4K_4[Fe(CN)_6]$ when pure salts are used [4, 5].

Potassium is determined as follows; a hydrochloric solution of the ash obtained from 3-10 g of organic material is prepared in the usual manner. The solution is transferred to a 25 ml standard flask and its volume made up to the mark.

Not more than 10-12 ml of solution containing 10-80 mg of potassium is taken for analysis; this amount is transferred to a test tube which has a mark at 15 ml, the solution is heated and neutral red added, MgO is then added in small amounts until the color of the solution changes from red to a weak yellow.

Calcium and magnesium phosphates are precipitated, as well as small amounts of Fe, Al, and Zn.

The solution is then allowed to become cold and its volume made up to 15 ml with water; it is filtered into a 15-20 ml measuring cylinder, 10-12 ml of this solution is poured into a test tube (fitted with a stopper) with a mark at 25 ml, and exactly 5 ml of 0.25 M $Mg_2[Fe(CN)_6]$ added (a more concentrated solution can be used, but in this case the volume of reagent added should be decreased accordingly).

After shaking, 8 ml of 96% ethanol is added, and, if necessary, water is added to bring the volume up to the 25 ml mark; the tube is shaken again and is then allowed to stand for 30 min for the precipitate to age. Four ml of water is added, or 3 ml if there is only a small amount of precipitate, the tube is shaken and the contents filtered through an

TABLE 1. Corrections to be Applied for the Precipitant Remaining in the Precipitate

Amount of potassium determined in the volume taken, mg	10	20	30	40	60	80
Amount of potassium that should be subtracted, mg	1,4	1,70	1,60	1,50	1,30	1,00

Table 2

Taken	Potassium, mg		Taken	Potassium, mg	
	Found in the precipitates:			Found in the precipitates:	
	After washing	Without washing but after applying corrections		After washing	Without washing but after applying corrections
15,0	14,7 14,9 } 14,8	15,7 15,9 } 15,8	50,0	50,1 50,3 } 50,2	49,0 50,8 } 49,9
25,0	25,0 24,4 } 24,7	25,5 25,7 } 25,6	75,0	75,1 75,3 } 75,2	77,1 76,2 } 76,6

ordinary filter paper 8 cm in diameter. The precipitate is quantitatively transferred onto the filter paper, using the filtrate itself, the filter plus precipitate are removed, placed on filter paper, and when the liquid has run off, they are pressed between sheets of filter paper until there is no observable trace of liquid on the paper; they are finally dried in a thermostat at 50-60° or in air until there is no odor of ethanol. The filter paper is opened out and immersed in a beaker containing 100 ml H_2O and 10 ml H_2SO_4 (1:3), the whole is then stirred with a glass rod until the precipitate dissolves; the solution is finally titrated with 0.05 N $KMnO_4$ until the color of the solution changes from yellow to brown; the color change at the end point is very sharp. One ml of 0.05 N $KMnO_4$ is equivalent to 3.91 mg potassium.

The precipitate obtained after squeezing out the liquid contains a small amount of precipitant which is titratable with $KMnO_4$, and accordingly the corrections given in Table 1 must be applied; it is also necessary to use filter papers of the same diameter (8 cm) made from ordinary filter paper.

The precipitate can be washed with a 10% solution of $MgCl_2$ in 32% ethanol; in this case there is no need to apply any corrections. This technique, however, leads to excessive use of alcohol, but the main disadvantage is that the time taken to carry out a determination is increased.

Table 2 contains results of the determination of potassium in synthetic mixtures of materials which occur in plant ash; the results were obtained on titrating washed and unwashed ferrocyanide precipitates with permanganate; in the latter case corrections were applied.

The experimental error does not exceed 6%. Ten potassium determinations can be carried out in 45 min.

SUMMARY

A simple method has been developed for the titrimetric determination of potassium in plant materials by means of magnesium ferrocyanide. The relative error for the determination of 10 to 80 mg of potassium does not exceed 6%.

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A TITRIMETRIC METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF VANADIUM

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A large number of titrimetric methods are known for the determination of vanadium. One of the most widely used methods is titration of quinquevalent vanadium with Mohr's salt; vanadium is oxidized to the quinquevalent state by means of permanganate, excess of which is removed by boiling with concentrated HCl [1, 2], or with sodium nitrite [3, 4]; excess nitrite is complexed with urea. Oxalic acid is sometimes used for removing excess permanganate [5]. Diphenylamine and phenylanthranilic acid are the indicators most frequently used. Vanadium which has been reduced to the divalent state by means of cadmium amalgam can be titrated with dichromate [6] or trypan red [7]. In addition to direct titration, back titration methods can also be used; vanadium is reduced with a known excess of Mohr's salt and the excess titrated with ceric sulfate in the presence of o-phenanthroline [4] or with dichromate in the presence of barium diphenylaminesulfonate [8].

There is also a large number of potentiometric methods of determining vanadium [3, 5, 10-15]; the chemical processes underlying these methods are the same as those considered above. Nevertheless, none of the methods indicated above enable microgram amounts of vanadium to be titrated.

Tests which we have carried out showed that microgram amounts of vanadium can be titrated in an acid medium by means of azo dyes. A spectrophotometric variant for the determination of small amounts of vanadium by means of azo dyes has been described previously [9].

In acid media azo dyes form brightly colored addition products (halochromic compounds); the mechanism of this reaction reduces to an acid - base interaction of dye with acid; in this connection, azo dyes have found wide application as acid-base indicators (methyl orange, naphthyl red, methyl red, etc.). The azo group $-N=N-$ is fairly active with respect to the action of reducing or oxidizing agents on it. In the first instance the reaction reduces to the formation of amino substituted azo- and diazocomponents:

$$Ar-N=N-Ar+4H=Ar-NH_2+H_2N-Ar$$

In the second case oxidation – reduction splitting of the azo compound occurs with formation of hydroxy substituted azo- and diazo components and liberation of free nitrogen:

$$X_1-Ar-N=N-Ar-X_2+4H_2SO_4+4HVO_3=$$
$$=X_1-Ar-OH+X_2-Ar\begin{matrix}OH\\OH\end{matrix}+N_2+4VOSO_4+5H_2O,$$

where X_1 and X_2 are the substituting groups.

We should like to propose methyl orange (other azo dyes can be used also) as a titrant for the quantitative determination of microgram amounts of vanadium. The reaction between methyl orange and vanadate proceeds fairly quickly in a strongly acid medium (H_2SO_4 concentration equal to 60% by volume).

On titrating 10^{-6}M vanadate solutions with a methyl orange solution it was established that the stoichiometric coefficients are in the proportion of 4:1 (Table 1). When the reaction conditions are changed the ratio of the coefficients may be different (e.g., 6:1).

When chemically pure methyl orange and sulfuric acid are used the theoretical titer of methyl orange can be accepted; otherwise the methyl orange must be standardized against ammonium vanadate, or even better against vanadium

TABLE 1. Titration of HVO_3 with Methyl Orange (concentration of the solutions 10^{-4} M)

v_1, vanadate, ml	v_2, methyl orange, ml	v_1/v_2	v_1, vanadate, ml	v_2, methyl orange, ml	v_1/v_2
4,00	1,04	3,84	8,00	2,06	3,88
4,00	1,02	3,92	12,00	2,98	4,02
8,00	1,96	4,08	12,00	3,04	3,94

TABLE 2. Determination of Vanadium in Steel (Standard Sample No. 124, 0.240% V)

Vanadium found, %	Deviation, %	Vanadium found, %	Deviation, %
0,235	0,005	0,242	0,002
0,250	0,010	0,243	0,003
0,245	0,005	0,246	0,006
0,238	0,002	0,235	0,005

pentoxide. The methyl orange should be standardized with ammonium vanadate immediately after dissolving an aliquot of the dye in 60% sulfuric acid; this is necessary because in strongly acid media NH_4^+ ions are gradually oxidized by VO_3^- ions.

So that the ratio of the volumes of methyl orange and vanadate should be near to unity, 10^{-4}M solutions of methyl orange and approximately 4×10^{-4}M vanadate solutions should be prepared.

Titration is carried out with methyl orange supplied from a microburet (2-5 ml) until a stable weak rose color appears.

Forty micrograms of vanadium can be titrated with satisfactory accuracy without interference from the following ions (in μg): Co^{2+} –100, Ni^{2+} –400, Cu^{2+} –250, Cr^{III} –300, Al^{3+} –3000, Zn^{2+}–10,000, Mn^{2+} –2,000, Fe^{3+} –50 (in the presence of H_3PO_4–15,000) Ti^{IV} –50, MoO_4^{2-}, WO_4^{2-} –40. Fe^{2+}, Bi^{3+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Br^-, NO_2^-, I^- and the oxidizing agents Cl_2, Br_2, MnO_4^-, CrO_4^{2-} etc, interfere with titration.

The method suggested has been tried out on a standard sample of steel No. 124 (Table 2).

Determination of Vanadium in Steel. 0.1-0.5 g of steel is dissolved on gentle heating in a mixture of 20 ml dilute (1:3) sulfuric acid and 5 ml of dilute (1:1) nitric acid. The solution is evaporated until copious fumes of sulfuric acid are evolved; evaporation should not, however, be carried out until salts start to separate out. After cooling, the residue is diluted with 100 ml of water, 3-5 ml of phosphoric acid is added, and the vanadium is oxidized by dropwise addition of 2% potassium permanganate solution until a rose color which is stable for 1-2 min appears. After the vanadium has been oxidized, 1 ml of 4% manganese sulfate is added and the solution titrated with 0.1 N oxalic acid. The decolorized solution is filtered if it is turbid, and the filtrate diluted to the mark with water in a 200-250 ml standard flask. 2-3 ml of the solution obtained is back titrated with a sulfuric acid solution of methyl orange.

SUMMARY

A titrimetric method is suggested for the determination of microgram amounts of vanadium; it is based on the redox reaction of vanadium with methyl orange; the brightly colored sulfuric acid solution of methyl orange acts simultaneously as working solution and indicator. The concentration of the working solutions is of the order of 10^{-4}M.

The method has been checked on a standard sample of steel No. 124, and gave satisfactory results.

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DETERMINATION OF HEXAETHYL DILEAD IN TETRAETHYL LEAD

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Even small amounts of hexaethyl dilead (HEL) present as an impurity in tetraethyl lead lead to instability of tetraethyl lead itself and of ethyl liquid prepared from it.

The following methods are known for the determination of HEL in tetraethyl lead.

1. Parallel use of the molybdate and iodometric methods with subsequent calculation of the amount of HEL [1]. This method is not suitable for technical control, since unsaturated organic products which can react with iodine may be present in technical tetraethyl lead.

2. Distillation of tetraethyl lead from its mixtures with HEL followed by determination of the latter on the basis of the specific gravity of the high boiling fraction remaining [2]. This method is complicated and involves numerous manipulations with such noxious materials as tetraethyl lead and HEL.

3. Determination of HEL in its mixtures with tetraethyl lead by spectrophotometric [3] and polarographic methods [4,5].

We have developed and checked on a method of determining HEL in tetraethyl lead which is based on the following reaction in acetone solution:

$$3Pb_2(C_2H_5)_6 + 2KMnO_4 \rightarrow 3Pb_2(C_2H_5)_6O + K_2O \cdot 2MnO_2$$

In developing this method we made use of Austin's observation [6] that tritolyl lead is oxidized by potassium permanganate with formation of the corresponding hydroxyl derivatives, and also of Bahr's observation [7] that triphenyl lead in the form of a suspension in acetone reacts quantitatively and instananeously with potassium permanganate, even at ordinary temperatures, to form the corresponding oxide. On the basis of this reaction Bahr suggested a method for the quantitative determination of triphenyl lead.

Experimental Part. HEL was prepared by Hein and Klein's method [8]. The HEL used was a transparent liquid with a lemon-yellow color and with a specific gravity of $d_{20}^{20} = 1.94\text{-}1.96$.

Tetraethyl lead was purified by two- and three-stream distillations of the technical product and had the following indices: specific gravity $d_{20}^{20} = 1.643\text{-}1.645$; $Pb(C_2H_5)_4$ content 99.0-99.8%.

Acetone conforming to GOST 2768-44 premier grade was used; it was freed from oxidizing impurities by boiling 600 ml of it with 20 g of potassium permanganate for 3 hr; it was finally distilled through a fractionating column.

HEL content of the tetraethyl lead, %	HEL taken, g	HEL found	
		g	% of that taken
26.57	0.2740	0.2733	99.7
2.93	0.1924	0.1957	101.7
0.0106	0.0018	0.0019	105.0

Standardization of the Solution of $KMnO_4$ in Acetone. The most suitable solution proved to be a 0.05 N solution of $KMnO_4$ in acetone, i.e., 100 ml of solution contained 0.2634 g $KMnO_4$. The solution was standardized against oxalic acid in the presence of sulfuric acid. Nevertheless, in calculating the value of the normality under the titration conditions used in neutral and weakly alkaline media, the value of the normality obtained by the method given above was multiplied by 3/5.

Study of the Interaction of Potassium Permanganate and HEL. A 0.08-0.2 g aliquot of HEL was placed in a 250 ml flask and 20 ml of purified acetone added; the HEL was then titrated with the acetone solution of permanganate with continuous stirring.

The reaction proceeds very rapidly – the permanganate color disappears immediately; the solution acquires a yellow color and becomes turbid. When titration nears completion, coarse, brown colored flocs which readily separate out are formed, and the solution becomes transparent. Titration can be considered complete when the liquid over the precipitate acquires a weak rose color on adding one drop of permanganate. On determining 0.1292 and 0.0944 g of HEL, values of 0.1320 and 0.0925 g were obtained.

HEL is therefore titrated completely; the deviation of the results obtained from the true value does not exceed 5%.

Behavior of Pure Tetraethyl Lead under the Condtions Used For Titrating with Permanganate. On adding the 0.05 N acetone solution of potassium permanganate to tetraethyl lead dropwise, the violet color disappears immediately, i.e. tetraethyl lead is oxidized. Nevertheless a different picture is observed when a dilute acetone solution of tetraethyl lead is used; the solution invariably acquires a rose color on addition of 1-2 drops of permanganate solution, this rose color being stable for 30 min and longer. This means that it is possible to determine HEL in tetraethyl lead by the method indicated.

Determination of HEL Present as an Impurity in Tetraethyl Lead. Solutions of HEL in tetraethyl lead were prepared for the work, the concentration of the former ranging from 0.01 to 26%. Five ml of solution (about 8.2 g) was taken for titration at concentrations up to 5%; smaller volumes of solution were taken at the higher concentrations. The sample was diluted with 20 ml of purified acetone and titrated with 0.05 N potassium permanganate with good stirring. The method permits determination of HEL with a relative error not exceeding 5% (see table).

A study was made of the effect of unsaturated organic compounds (which may be present in industrial tetraethyl lead) on the results of the determination of HEL in tetraethyl lead.

Olefines are oxidized by permanganate. On titrating a number of unsaturated compounds in acetone with permanganate, it was shown that oxidation is very slow. Since HEL, as noted already, is titrated immediately, then, as a number of tests showed, the presence of unsaturated organic compounds which react slowly with permanganate has almost no effect on the results of the determination of HEL.

Analytical Procedure: 5-10 ml of clear, sediment free technical tetraethyl lead is introduced into a flat-bottom flask; it is diluted with 20 ml of purified acetone, and is titrated with a 0.05 N solution of permanganate in acetone, the contents of the flask being mixed by a rotating movement. When the first 1-2 drops of $KMnO_4$ gives a rose color which does not disappear for 5-6 sec, it can be considered that there is no HEL in the tetraethyl lead. When the rose color disappears immediately, being immediately replaced by a yellow color, titration is continued until a rose color appears which is readily observable on a white background.

One ml of 1 N $KMnO_4$ is equivalent to 0.2944 g hexaethyl dilead.

SUMMARY

A method has been developed for the quantitative determination of hexaethyl dilead in tetraethyl lead in the presence of unsaturated hydrocarbons, the hexaethyl dilead being present as an impurity. The method consists in titrating an acetone solution of tetraethyl lead with a 0.05 N solution of potassium permanganate in acetone.

The experimental error of the method is 5-10% (relative). The method is sensitive down to 0.01%.

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"The Analytical Chemistry of Thorium" by D. I. Ryabchikov and E. K. Gol'braikh, the book under review, is one of a series of monographs which the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR intends to publish under the general name "The Analytical Chemistry of the Elements." There is hardly any need to dwell on the very great necessity for and the very earliest publication of a series of monographs in which is brought together all the factual scientific-methodological material and the vast practical experience accumulated by many thousands of research and practical workers in the field of analytical chemistry both in the USSR and abroad. Such an analytical encyclopedia will favor the further development of this important branch of science, and its practical application to solving all the complex problems in the field of the analytical control of modern production.

The fact that the authors used 2142 literature sources published in the USSR and abroad during 1957-1958 testifies to the huge amount of work carried out by them in compiling this monograph.

The monograph comprises five chapters.

The first is devoted to information on the general and inorganic chemistry of thorium.

The second chapter is devoted to descriptions of the chemical and physicochemical methods of determining thorium, these being prefaced by qualitative reactions for the thorium ion.

A considerable amount of attention is given to the complexometric method, which can be regarded as a fundamental method. Questions relating to the theory of complexometric titration and the indicators used are considered here, and actual methods of determining thorium are described. Titrimetric, spectrophotometric, and volumetric high frequency methods of determining thorium by means of sodium ethylenediamine tetracetate are also described.

Consideration of photometric methods of determining thorium is preceded by an outline of some general theoretical premises relating to the development of colored reaction products formed during the interaction of thorium ions with organic and inorganic reagents.

It is pointed out that polerographic methods of determining thorium have not found practical application. An indirect amperometric method of determining thorium is described. Spectographic, x-ray spectographic and radiometric methods of determining thorium are briefly outlined.

Separation of thorium from accompanying elements forms the subject of the third chapter.

For separating thorium from the rare earths, use is made of methods based on differences in the chemical and physical properties of these elements (basicity, solubility of their respective compounds, their complex-forming capacity etc). Chromatographic, extraction and other separation methods are considered.

In addition, methods are described for separating thorium from scandium, titanium, zirconium, uranium, iron, aluminum, niobium, tantalum, silicon, and phosphorus and from lead and other metals of the hydrogen sulfide group.

The fourth chapter is devoted to methods of determining thorium in natural and industrial materials, including alloys. Regeneration of thorium from industrial wastes is also described.

Methods of determining impurities in technical and high purity thorium are considered in the fifth chapter. Methods of purifying thorium from uranium-233, protoactinum-233, and radioactive fission products are also described in this chapter.

Of considerable use are the literature references on the synthesis of the various reagents required for carrying out a particular method of analysis; this will help our analysts to make wider use of new analytical methods for determining thorium.

Though this review of the contents of the monograph is of necessity brief, it nevertheless gives a fair idea of the huge amount of material that it contains.

Bearing in mind the fact that many, if not most of the reagents, and the conditions under which they are used, turn up during consideration of the methods of determining thorium (Chapter II), during consideration of the methods of separating thorium from other components (Chapter III), and also during consideration of methods for determining thorium in natural and industrial materials (Chapter IV), it does strike one that it might be better to bring together all three applications of any reagent that turns up repeatedly in the general theoretical part of the monograph, with the aimof greater compactness and for making it easier for the reader to obtain the information he wants on any particular reagent he is interested in. There is the possibility, however, that should this be done, it might be difficult to achieve the requisite separation of the fundamental analytical methods, and to deal with them sufficiently fully.

Moreover, in order to avoid frequent repetition, resort should be made more often to reference to previous sections of the monograph in which any particular reagent or method has already been dealt with.

A large number of methods for determining thorium and the reagents used for this purpose, are described in the mongraph, and the sensitivity, accuracy, and effect of other elements are considered; methods of removing the latter are also included. Many of these methods are very similar to each other with respect to these analytical characteristics, i.e., sensitivity, etc. Accordingly, it is very difficult for the analyst who is making his first acquaintance with the analytical chemistry of thorium to assimilate, critically evaluate, and select the best method from the vast amount of material collected in the book under review, without having the general characteristics, and a comparison of the advantages and disadvantages of each method before him.

In order to get a more rapid idea of the advantages of some methods and the drawbacks of others, it would obviously be very useful to include tables at the end of each chapter (or in the appendix) containing the most important characteristics of the methods with respect to their fundamental indices.

Having completed an examination of this monograph, the reviewer must express the great satisfaction which he had derived in reading it. This monograph on thorium is a serious contribution to Russian literature on the analytical chemistry of the elements, it will be of great service to analytical chemists in scientific-research and industrial laboratories.

One must express the hope that the material in the reviewed monograph (just like that in the other monographs in this series of the "Analytical Chemistry of Elements") will be periodically supplemented by systematic critical reviews of the literature.

A. M. Dymov

G. Charlot, LES MÉTHODES DE LA CHIMIE ANALYTIQUE

ANALYSE QUANTITATIVE MINÉRALE

Paris, Masson et Cie 1961, 1024 pp., 4th ed.

**Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 4,
pp 511-512, July-August, 1961**

G. Charlot's book consist of two parts.

The first part is devoted to the theoretical bases of analytical chemistry. The material is classified as follows: 1) chemical reactions in solution; 2) electrochemical reactions and voltametry; 3) measurement methods; 4) various methods and techniques.

The second part is devoted to selected methods of determining a large number of elements, methods which have not only been tried out in the author's laboratory, but also by the Commission on Analytical Methods of the Commissariat on Atomic Energy, by the French Standardization Association, by the analytical chemistry section of the French Chemical Society, and also by some industrial societies. Methods of determining all the elements with the exception of the inert gases and radioactive elements (apart from Tc, Th, and U) are considered in this part.

In Section I of the first part, the reactions of acids and bases, oxidizing agents and reducing agents, and precipitation reactions (including homogeneous precipitation) are considered in general terms; the concepts of extraction and its practical application, distillation, and coprecipitation are advanced; various types of chromatographic techniques and their practical application are considered. In addition, the dissociation constants of acids and bases, the apparent instability constants and the redox potentials are included.

Section II is devoted to a qualitative and quantitative interpretation of the results of electrochemical reactions and to the theory of electrolysis. The nature of the current - potential curves is discussed, as well as the effect on them of various factors in the course of chemical reactions when various electrodes are used; the techniques of the practical use of electrolysis and electrography and reduction by metals and amalgams are discussed.

The theoretical bases of various methods used in analytical chemistry are outlined in Section III, and these methods include spectrophotometric, luminescent, thermogravimetric, radiometric, etc. Various titrimetric methods are considered: potentiometric, amperometric, coulometric, photometric, radiometric, complexometric tensiometric, and many others. The material on polarography is presented in the chapter devoted to amperometry. Both widely used, as well as new reagents and indicators used for pH determination in redox reactions, etc are discussed. Finally the bases of emission spectrographic analysis and spectrophotometry are outlined.

Section IV is devoted to the properties of ionizing and non-ionizing solvents, and their practical use in neutralization, complex formation, and redox reactions.

Chapter V is devoted to the question of determining traces of elements, preparation of samples, dissolution of samples, and the destruction of organic materials by wet and dry methods. In addition, the sensitivity limits of the methods are given. In the sections devoted to the analysis of gases, and also to those on semimicro- and microdeterminations the author limits himself to published sources.

The characteristic way in which the material is outlined in this interesting book distinguishes it from other textbooks on analytical chemistry. It has been written very clearly, the newest scientific data being taken into account. Complexometry, titration in nonaqueous media, electrochemical reactions, various new titration techniques – thermochemical, polarometric, refractometric, cryometric, gasometric – electrochromatography, spectrophotometric titration, statistical treatment, microbiological analysis, etc are all well treated. Particular attention has been given to the quantitative determination of such elements as U, Th, Ti, Zr, Nb, Ta, B, Be, etc.

The textbook includes 392 diagrams, many of which are original and illustrate the theoretical material graphically. References to published original work and reviews are included in each chapter.

It would be correct to say however (incidentally, with G. Charlot's agreement) that the book is not perfect. Subjects of similar themes are separated in many instances. We think that questions relating to the theory of electrochemical reactions and voltametry should not be separated from amperometric, potentiometric, and similar analytical methods. Material on radiometric determination should be linked with the expostion of radiometric titration. Methods of separating and methods of determining the elements should be separated more clearly. One must regret that physical methods of analysis are hardly dealt with at all.

On the whole G. Charlot's book is, undoubtedly, of great interest not only for analytical specialists, but can also serve as a reference book and textbook for aspirants and students, and should be translated into Russian.

D. I. Kuznetzov

A NEW REAGENT FOR THE DETERMINATION OF CADMIUM - BROMBENZTHIAZO

Translated from Zhurnal Analitichesko Khimii, Vol. 16, No. 4,
back cover, July-August, 1961

A new reagent for the colorimetric determination of cadmium –brombenzthiazo– has been synthesized at the All Union Scientific-Research Institute of Chemical Reagents and Special High Purity Chemicals (IREA).

The new reagent has approximately the same sensitivity and selectivity as dithizone, but has the advantage over the latter that it is simpler to use and is more stable.

Organizations and enterprises wishing to test the new reagent may obtain a free sample, and instruction for its use, by applying to the address: Moscow E-61, Bogorodskii Val, D. 1, IREA. It is requested that a report on the practical value of the new reagent be sent to IREA within a two month period after receiving the reagent.

The Institute will advise on all questions relating to the use of brombenzthiazo.